The Journal
of the
SOCIETY OF DYERS
AND COLOURISTS

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Proceedings of the Society

SCOTTISH SECTION

Meeting held at the St. Enoch Hotel, Glasgow, on 17th January 1950
Mr. E. D. KENNEDY in the chair

On Reading the *Journal*

R. A. PEEL

No sooner had everyone become comfortably seated than packs of playing cards were distributed and before long several schools of contract bridge had been formed. Some of the "lighter spirits" played vingt-et-un or poker, whilst a party at one table played a game which was suspected to be "Old Maid".

. . . The prevailing tiredness was reflected in the fact that Miss Evelyn Laye walked almost unnoticed through the hall of the hotel.

You may think that this is from the pages of the *Tatler*— but no! it is a quotation from the 1938 *Journal*, the "Whitsuntide Tour of the Society by Invitation of Imperial Chemical Industries Ltd."[1] I am glad to quote it— a daring incursion into frivolity— far from to-day's atmosphere of highly refined theory. I quote it because I rebel at the higher mathematical, physical, and chemical substance of our *Journal* to-day. In correspondence in the *Journal*, Neale[2] has said—

. . . It cannot yet be contended that dyeing has become a branch of theoretical physics, or that the behaviour of a dyebath can, like that of a hydrogen atom, be predicted by means of pure mathematics from a small number of *a priori* assumptions. The theoretical treatment of dyeing, like that of some other branches of science, is in some danger of getting into an unhealthy state of hothouse growth, with too much superstructure but with insufficient roots in the solid ground of experimental fact.

. . . if we have to jettison factors which, though theoretically desirable, are not yet ascertainable by experiment, then let us do these things at the outset, and so save our readers unnecessary expenditure of thought.

Now, having delivered a broadside, I propose to disengage, although there may be a whiff of grape-shot at similar targets later on.

READING

Let me confess that my own reading of the *Journal*, prior to my decision to speak on reading it, had been somewhat desultory; of course, I have always read with attention those parts which I considered useful to my own work, that is the production of dyed rayon piece goods.

After twenty-five years of membership, and therefore twenty-five years' reading, I am amazed at the good reading I have missed; the re-reading of such has been a delight. I am not surprised, however, at some things I have missed— I still continue to miss them— long abstract communications containing much abstruse and theoretical reasoning, these I barely read at all; these are study, and require a student's concentration— yet as a junior member of the Society I, too, was a student, and doubtless in those days I studied such work, though if I remember aright my object was to pass the necessary examinations, and swotting was necessarily based on a lecture programme. This left little time, coupled with apprenticeship duties, for a deep reading of the more difficult parts of the *Journal*.

The ever-increasing unwieldiness of dyeing knowledge compels discrimination of what to read and what to reject. We tackle one subject when studying— in reading it is wise to do similarly, but read for interest rather than profit, and therefore cultivate a wider appreciation of the dyeing scene. I feel that, whilst one can read all the *Journal* as it is issued month by month, it is difficult to understand what one has read without risk of mental indigestion— which brings me to the art and practice of reading the *Journal*.

My own habit month by month is to dip and skim, and pick and choose, and then really "Have a Go" with what takes my interest. I wonder occasionally how others read the *Journal*— this one turns straight to *Situations Vacant and Wanted!* another, say a dyestuff supplier, looks carefully at his own and his competitors' advertisements and then at the *Manufacturers' Pattern Cards* page. Perhaps another may be in no hurry to read his *Journal* at all, and it may lie a sealed cylinder as when it was posted, collecting dust with its like.

It is right and proper that we should accumulate all the dyeing and chemical knowledge we are able, but we know it is impossible to absorb all the

abstracts and follow them up by reading all the originals. It is impossible to follow all the communications or the reports, and the Editor and the Publications Committee know this— they have to cater for all types— "You pays your money and you takes your choice", in other words you select, and if there is a preponderance of any particular work your selection will be narrowed accordingly.

My protest is that the mass of pure knowledge accumulating in the *Journal* is becoming frightening; if there is a paragon who understands it all, he must be even more frightening. We need to pause, to revise, to point the way, to make the road of the "doer" easier. Of course, we can never stand still, but surely we can rest on the way, or we will never reach the heights in condition to master new horizons. Sir Henry Tizard has said in his challenging 1948 Presidential Address to the British Association—

> All social progress such as the spread of education, promotion of health, opportunities for leisure, and healthier recreation, must depend upon the power of science and technology to increase the productivity of industry. The rate of social reform is set by the rate at which productivity increases, and social unrest is inevitable if reform lags too far behind the advance of technology or is pressed too thoughtlessly before it. So we must judge the effect of industrial research, not merely by the new comforts and luxury that it produces, but also by the rate of improvement of existing processes.

More practical and technological papers are needed in our *Journal* to bring about this improvement.

EDITORS

The *Journal* owes its success to its editors, and our Society has been blessed with a succession of fine editors, Knecht, Gardner, Rowe, Clayton. It has been said of Professor Knecht— "His heart was in the work with no thought of personal credit"[3]. Knecht's life-long work for the Society has been recognised, and the *Journal* to-day bears his escutcheon.

THE BEGINNINGS

The Jubilee issue of the *Journal* published in 1934 covered the history of the Society, and reading the old numbers emphasises the practical yet scientific outlook of the founders. For instance, in Volume 1, No. 1 (25th November 1884) we read—

> The *Journal* will be under the direction of an Editor, supported by a Publication Committee in which every branch is represented by specialists. The chief object will be to keep the Society informed of new work done here and abroad, by means of abstracts from scientific and technical journals, English and foreign, and with the assistance of foreign correspondents specially selected.

and in the first issue also[4]—

> If a dyer is asked what are the main qualities which he expects from any novel colouring matter presented to him by the colour manufacturer, his answer will probably be: "It must be cheap, easy of application, and fast".

The forthright thinking and speaking of those days is illustrated in the discussion on Mr. Hummel's paper[5]—

> The CHAIRMAN (Mr. Sharp): . . . Mr. Hummel's paper will be . . . one containing a very uniform mixture of scientific knowledge with practical application.

Therefore it offers many advantages as a paper to practical men. We are not led into a fog with any very complex formula, neither have we the practical points which are valuable to practical men left in abeyance, . . ."

But you must not believe that these early issues contained only sturdy common sense (that term has a reminiscent tone about it!). Dr. F. H. Bowman, in lectures at Bradford and Huddersfield on *The Structure of the Wool Fibre and its Relation to the Use of Wool for Textile Purposes*, gave for the first time information as useful to-day as when it was published in 1885. These lectures, marvels of description, gave much knowledge new to that age[6]. Bowman also said this—

> All our machines and processes are only a means to an end, and the correct method of proceeding is ever to have the end in view from the beginning.

A Churchillian phrase!

PIONEERS

I have mentioned names, and though many who have helped to build the *Journal* cannot in this short essay be mentioned, they are not forgotten; we know the work they have done, and are doing— and we thank them for it! There are other nameless ones commemorated by a fine contribution in the 1940 *Journal* entitled "A Retrospect"[7].

What a wealth of material for communication to the *Journal* we have in the lives of those who built it! Think of the names— Hickson, Meldola, Green, Wardle, Pullar, Thorp Whitaker, Holliday, Sharp, Levinstein, Douglas— and here I must pause a moment— much is deservedly known of the great scientists, their names are commemorated in lectures such as the Mercer, and medals such as the Perkin. I am glad to see another name honoured, that of George Douglas, a pioneer just as Perkin and Mercer, a pioneer of the new joint stock companies, a welder of human personalities, a binder of the most independent individuals known into an internationally famous dyeing organisation— a dyer, a business man, an educationist, a trainer of apprentices who have manned the dyehouses of the world, and a Founder Member of this Society and a former President.

DEVELOPMENT

How has the *Journal* developed? Surely from the practical to the scholarly, but above all it has grown in range; the 1949 Annual General Meeting described the remarkable increase in all kinds of dyeing and colouring publications in the *Journal*. I think that the 1939 *Journal* provided a vintage year, for we had speeches by Baddiley, Dreyfus, Levinstein; there were the chemistry of cellulose, the life of Hummel, and the first publication for members of the physical and dyeing properties of nylon. Perhaps owing to the stress of war and preparation for war many could not read it— indeed my own pleasure has been greater in re-reading it to-day because obviously I had not absorbed the half of it.

A notable recent feature has been the symposia and summer schools; these have presumably one object in view— the promotion of knowledge of our craft. Listen to this epitome of the Manchester Summer School 1948[6]—

Summer Schools and Refresher Courses in scientific and technical subjects have become fashionable in recent years. The fashion has arisen in most cases from a real and important need, for new fundamental discoveries, experimental techniques, and industrial processes are multiplying with ever increasing speed. . . . To carry on this development [of a detailed and satisfactory explanation of the mechanisms of dyeing] requires an extensive and up-to-date experience in mathematical physics and physical and organic chemistry— to understand what is going on should need only common sense. But Blackpool was a new version of the Tower of Babel, for the practical men did not always understand the language of the scientists.

. . . These dyeing and printing actions, seen in the gross in industrial operations, are but the summation of processes taking place on the molecular scale and, where the information is available, capable of being seen, in outline at least, by the mind's eye. Much of the time during these lectures was spent among the fibre molecules watching the dyes go in and out. Perhaps some of the later views of these regions given by the electron microscope will show that we were living in a dream-world, but it was very stimulating nevertheless.

BIOGRAPHICAL

Biography is usually readable, and the lives of Hummel, Green, and Perkin have given me much enjoyable reading. From Rowe's classic[9] we learn how Perkin was the first to develop the now general method of dyeing silk in a soap bath, and, of particular interest to us in Scotland, of his work with Robert Pullar in Perth and his successful dyeing of Mauve in Dalmonach Print Works, Alexandria, which probably originated the practice of supplying the colour user with technical service.

We read in Walker's prize-winning paper[10] how Hummel started his industrial career in 1870 at the Calico Print Works of James Black & Co., Alexandria, where he remained until 1876 carrying out important research, and the development of the dyeing and printing of basic dyes on tannin–antimony–tartar emetic mordant. Whilst at Alexandria Hummel ceased to use Madder and substituted the then new artificial Alizarin at far less cost. Hummel's first experience of teaching (which was to take him to the Dyeing Department in the Yorkshire College) was gained whilst conducting free evening classes for the dyeing and printing apprentices of Alexandria.

I can only quote part of the prologue and epilogue of Saunders' paper, *The Scientific and Technical Work of Professor A. G. Green, F.R.S.*[11]—

To recount the achievements of a great man is labour lost unless the work sheds light to guide the efforts of lesser men. Moreover, in these days when research and invention have risen to the level of a profession, the question is often debated as to whether success is due to temperament and chance alone, or whether team work linked with conscious planning can sow the seeds of an assured success.

And the final words—

. . . There are chemists who decry the study of history, even that of chemistry itself, on the ground that the past is dead and gone, oblivious to the fact that, whether they choose to know it or not, history determines the greater part of the unconscious content of their own minds.

HISTORICAL

In a lecture read before the Manchester Section in 1926 entitled *Reminiscences of the Dyeing Trade 1869–1925*, W. H. Pennington[12] paid tribute to the early dyers. He said—

The application of the available colouring matters was in the hands of men of moderate general education and limited chemical knowledge. The teaching of dyeing had not then been recognised as a branch of scientific or technical training . . . text-books were few, and what existed were almost beyond the range of the student. With all these disadvantages, the dyers of that day were, as a rule, shrewd and observant men . . .

While we have great hopes for the future, let us not forget the labours of the men who have passed away, especially of those men, who, groping through error into light, laid the foundation of our craft.

Again in Manchester, nearly twenty years later, the evolution of block and roller printing was discussed. I quote Beton[13]—

We are all familiar with the perennial craze for novelties, particularly textile novelties. The attitude of mind which this craze insidiously begets can be very well offset, or neutralised, by a proper sense of tradition, and by an informed curiosity about our predecessors. . . . it is probable that nowhere is the sense of continuity more profitable, or more conducive to interesting study, than in the hand-block industry, where many of the old ways still persist, where the printer-craftsman still plods along, with all the skill and patience of his forbears.

and Heaton[14] on *The Evolution of Styles in Calico Printing*—

. . . printers gradually acquired confidence and independence, and there were established two styles which have been the backbone of calico printing practically into modern times, viz. the Indigo style and the dyed Madder style. . . .

The industrial revolution, besides bringing abundant cotton cloth which was cheaper and more regular in quality (a very important matter for the calico printer) than ever before, produced the roller printing machine with its vastly increased output. Together, these factors created a demand for shorter process, more direct methods of application and greater variety of dyestuffs.

Both these extracts are admirable examples of a competent style which gives good reading.

Is there any thing whereof it may be said, See this is new? It hath been already of old time, which was before us.—(*Ecclesiastes* I–10).

Julius Hübner[15] made a special study of the history of dyeing— what he reported on Scottish dyeing history is closely related to events to-day, e.g.—

In 1552 an Act of Parliament was passed limiting the number of coloured cloths to "scarlet, red, crimson, murray, pink, brown, black, green, yellow, orange, tawny, russet, marble, grey, sadnew colour, asemer, watchett, sheep's colour, lion colour, motley, or iron grey".

Compare these with the standard shades laid down by law in recent years.

The "Scottish Cloth Manufactory" was founded at New Mills in 1681, and Hübner was able to examine authentic records which make piquant reading. I have extracted the following and added headlines—

IT'S EASY AND CHEAPER WITHOUT A DYER ANYWAY

. . . "it is to be considered what way blacks and reds may be dyed to save the charge of maintaineing a dyer."

IS IT SO EASY?

. . . "ordered that directions be given to the master that care be taken that the next reds be a better brighter color."

FOR MENDING FREE OF CHARGE

. . . "Robert Blackwood haveing had five ells dyed at New-Millns quhich he complains of as being damnified

in the deying . . . they ordaine him get back his cloth
without paying any thing for dyeing."

WE CAN'T DYE IT, SEND IT TO "SO AND SO"

. . . on December 13th, 1682, it was "ordered thatt
the next parcell of silk be all dyed att London except
what is for black quhich is alsoe to be boyled off there
as well as can be."

To conclude this portion of my reading it is
obvious that in 1682 as in 1950 the employer liked
to know as much as possible about his prospective
new dyer, persuade him from his job, and then
bind him with a contract—

In minute 505 instructions are given to induce a dyer
at Kinross to enter the services of the company:—
"That Joseph Young be desired to speak with the dyer
at Kinross to try his humor, character, pairts, knowledg,
sobriety, how he is imployed if he would remove and
for what."

In minute 523 it is stated that the dyer at Kinross
had been willing to change his position: "that Joseph
Young write to the dyer at Kinross to come south that
we may conclude with him," and in 536 "he writt to
John Home the covenants with John Bairns the dyer."

OBITUARY

Obituaries are of high standard in our *Journal*.
As good examples I commend Ellis Clayton on
James Ashton[16] and Sir Gilbert Morgan on Edward
Lodge[17]. (I can assure members who one day may
be worthy of such an honour that they will be well
looked after!)

PLAIN ENGLISH

I remember reading in *Endeavour* an editorial
gently chiding the scientist's lack of a good flow of
English. Now I am no critic, but we have in our
Journal occasional work which might be described
as good style. For instance, Haller, in a communi-
cation *Textilosophy*[18], goes on to visualise what
might happen when the cellulose of nature, pre-
sumably as trees, is exhausted. Whittaker answers
this in a typical letter[19]. The rhythmic communica-
tion and its practical answer could well form the
subject of a debate.

In 1937 an iconoclast who was to become a
President startled the Society. He criticised in a
flow of fine English much of the accepted dogma
and direction, and for long afterwards references in
the *Journal*, and the direct results which followed,
showed how much this blast of fresh air was
needed. I can only make one quotation[20]— it is
advice to individual members as well as to the
Society—

It was said recently of a French General that he
possessed a complete technique for his position in that
he had the knowledge and ability for doing the job well;
and in addition the technique of gaining the reputation
of being the man who knew how to do the job. Both
are important, and there have been more failures by
reason of persons not knowing the technique of creating
the reputation for doing the job, than by failing in the
job itself. Here, too, in my opinion, is a moral for us.
We hide our light too much under a bushel.

MORE INTERESTING READING

Our *Journal* has surely room for more of the
romance which is associated with colour, readable
articles covering processes of the past such as
Madder and Indigo— or the early attempts at vat
dyeing— I do not mean a plain catalogue of
methods which failed or succeeded, but a story of
the main scientific background, yet giving the
human relationships involved. I plead for plays,
scripts suitable for broadcasting, essays, and his-
torical notes vividly written— all based on our
craft. What has been written in our *Journal* in
recent years on the growth of the *Journal* and its
future? The fiftieth year certainly produced a fine
Jubilee edition, and the *Journal* has covered the
main developments of, for example, viscose, nylon,
and dye manufacture. I still plead for a regular
contribution which is readable and interesting;
such reading would be a refreshment, and would
stimulate the study of those articles to which we
refer in order to keep up to date with new pro-
cesses and inventions.

Perhaps some eyebrows were raised when I
mentioned plays and scripts. I have a booklet,
Mauve and Magenta, published by Pullars of Perth
— the script of a twenty-minute "Broadcast for
the Forces"— elementary, perhaps, by Third Pro-
gramme standards, but good listening and good
education. I should like to see something similar
published in the *Journal*. The history of Turkey
Red alone is packed with action and drama; who
will write it?

Shakespeare realised what was wanted; unique
master of his craft, he knew that the finest phrase-
ology, the most cunning and nimble verse, would
eventually tire the keenest of his audience. He
gave them light relief, and at the same time satisfied
the groundlings. From a host of ordinary folk
he created characters, which delight us still: think
of Shallow, Falstaff, and Quince— Shakespeare was
not afraid to "popularise". I use that word because
there is perhaps a fear[21] that, if the *Journal* is too
abstruse, we might attempt to "popularise" it.
Let us ask ourselves: "Is the *Journal* not becoming
too highbrow?" I am sure the Society would still
retain its high status in the dyeing and tinctorial
trades if it embellished its "blue stocking" reputa-
tion with an occasional multicoloured garter!

TECHNOLOGY

Though I have asked for more technological or
practical papers in the *Journal*, that is not to say
that this important service has been neglected. In
May 1939 at a meeting of Sectional Officers of the
Society we read of a desire for publication of more
practical papers. It was reported that there was
great difficulty in getting these— the Editors
would be pleased to consider papers of this type.

According to Levinstein[22] in his George Douglas
lecture—

Sir Henry Tizard said that . . . we were most back-
ward in the application of scientific knowledge to
large-scale production, . . . The main cost of industrial
research is not in the laboratory but in application to
the large scale.

Cannot the Society form a committee to deal with
modern technology— cannot our *Journal* publish
practical details of the application of new dyeing
and finishing processes, for example? Of course,
there are the great research associations, which
cater for their members with practical advice and
technical help. Similarly the dyemakers and rayon-
manufacturing concerns are liberal with technical
assistance. But our *Journal* should give a positive

lead, and not be so wrapped up in theory that it neglects the crying need of to-day in the dyeing and colouring industries— better technology, which means better workmanship. Surely the "George Bernard Shaw" of our Society would not have been urging the use of common sense throughout the years if it were a commonplace commodity? We know that Dr. Whittaker's publications have been of immense benefit to all in the rayon-dyeing trade. My only criticism of practical papers in the *Journal* is that there are not enough of them.

ECONOMICS

Neither is there enough published on the economic and costing side of our industry— with exhortations on every hoarding to increase production and keep down costs, the *Journal* should have something more to say. In 1926, T. D. Buttercase[23] gave a paper on *Dyehouse Economics*. I must quote from it, because it is still "hot news" twenty-four years later—

> In a typical dyehouse trading account, whether cotton or wool, the main items of expenditure in the order of their importance are— (1) Wages; (2) materials (dyewares, chemicals, fillings, &c.); (3) coal and power; (4) repairs and maintenance; (5) miscellaneous (including damages and allowances and all standing charges, rates, insurance, &c.).
>
> It is safe to say that even in the most efficiently conducted concerns there is a considerable margin of avoidable waste under each of these heads, and it may be that in the dyeing trade as in industry generally in this country we have not as yet fully appreciated the importance— nay the absolute necessity— of eliminating every possible form of waste. . . .
>
> The main trouble is— how are we, in the absence of a uniform system for the calculation of costings, to arrive at a sound basis of cost? Sooner or later the necessity will be appreciated. I therefore commend those in responsible positions in the industry to be thinking out this problem if only on the principle that the secret of successful organisation is anticipation.

I recommend that this stimulating lecture and the subsequent discussion be re-published, and correspondence invited.

HUMAN RELATIONSHIPS

What is the *Journal* doing at present in the way of a psychological approach to the vastly changed industrial conditions since 1884? Promotion of knowledge in the dyeing and tinctorial industries cannot ignore this vital problem. I believe we are putting the cart before the horse in devoting so much space in the *Journal* to dyeing theory.

THEORY

This brings me to a highly theoretical and controversial subject, *Colour Control*, in a paper[24] on which an analogy from engineering, the exact measurement of 1-in. bolts, is used.

Why should colour be absolutely measured within certain limits (e.g. ± 0.005)? A bolt is presumably a bolt to all who can see, and "red" as a colour is obvious as such to all but the colour-deficient; yet the degree of redness in the mind of the observer will depend on how his brain interprets "red". Colour is closely allied to the emotions and to the senses; therefore a "red" pattern can hardly be described by a series of numbers— one cannot judge distances under the influence of alcohol, similarly how can one standardise "redness" if one is under the influence of "red"? and I am not referring to after-images. In brief, how can we describe the quality of the sensation known as "red"?

Robert Burns wrote— "My Love is like a red, red rose". Perhaps some physicist of the future will describe his passion thus— "My platonic friend resembles colour number X units plus Y luminosity. It is interesting to note that this colour combination is remarkably close to the now obsolete red rose shade once referred to by poets."

The dyeing industry as it affects the consumer cannot be gauged by engineering standards, and when every colour and tint become standardised, every method becomes scientifically right, and no empirical trials are tolerated, then the trade can indeed be compared with the manufacture of bolts.

The great fashion experts such as Digby Morton, Hartnell, and Dior have a flair for colour, form, shape, handle; in other words, something to be sensed. Is it not typical of the brave new world we are to be led into that the glorious sensation of colour should be described in numbers? But I have not finished. Proper organisation of colour, we are told, would demand testing stations (central)[24], for the settlement of matching disputes, for example. This was suggested in 1940, and certainly this argument was not continued in the Mercer lecture on *Colour*. To-day in 1950 planned organisation is with us— there are testing stations for "eggs"! Can you not easily imagine the fate of your bright new "mauve" of 1962? Before it can be dyed for the public, before it can delight the fashion-conscious Paris as its predecessor, Perkin's Mauve, did one hundred years ago, it has to go to a Central Testing Station to be analysed and registered and numbered, until weeks later it is returned flatter in shade, with all its glory departed. In the meantime some "backyarder" outside the control has captured your market with his own new sparkling "mauve". Let us hope there will always be this individualism, this understanding of our trade as something of art, craft, beauty, joy, and life rather than as abstract science.

AFTER-DINNER SPEECHES

Annual Dinners have given some wise and witty reading— reports of these and similar functions could well form an *Anthology of the Great*, and I can quote only briefly from them. Unfortunately the Glasgow Annual Dinner (1949) is very sparsely reported when compared with others.

In 1938 Sir Percy Ashley was reported[25] as saying that it was some five centuries since the first handbook to the dyer's craft was published in Europe; it was not much short of that time since the craft received its first state recognition by the grant of a Charter to the Dyers' Company in London. Later he quoted the saying of a great German poet and philosopher that "every individual colour makes on men an impression of its own, and thereby reveals its nature both to the eye and to the mind."

And a sparkling toast to "Allied Societies" in 1926 by Principal B. Mouat Jones[26]—

> ... How, with all mankind their debtors, could the dyers and colourists single out individual sections or individual societies and say, "These men are our allies," when all men were their friends? Nevertheless, there were some societies with whom they might claim a special intimacy and consanguinity. Such was the Chemical Society, which fostered the study of the science which was the basis of the dyer's craft, and the Society of Chemical Industry, which translated the portentous verbosities of the pure chemist into the productive efforts of the strong, silent, and impure technician.

In 1940 Dr. C. T. J. Cronshaw, the President, said[27]—

> ... After all, we have been in existence for more than 50 years, and that, at all events, argues that we fill a distinct place and we must continue to do so. We must, therefore, have, very intensely, the will to persist. First of all we rely upon the continual and unqualified support of our members. ... We must maintain and even increase the quality and the reputation of our *Journal*.

And finally—

> ... One can imagine the eye, and that part of the brain over which the eye is master, laughing long and happily when the splendid shades of Red cause the optic nerve to vibrate.
> ... This commercial age is a wonderful period of the world's history, but it lacks much. It is practical, but often forgets the line of beauty.

Who said this? H. Gordon Selfridge, at the Annual Dinner of the Society in 1931[28].

I should like to say more (if I had space) about abstracts and reviews, the value of reprints, the importance of correspondence, the beauty and utility of type and printing, and the wonderful advance in advertisement— particularly in the splendid coloured advertisements, which reflect great credit on their sponsors. And lest we forget, we are able to read the *Journal* because of the great efficiency of the Society's servants and the voluntary labour of so many of its members.

And now, as Dr. Bowman would say, Recapitulation!

I have attacked the tendency to theorise, I have asked for more technology, and if my opening was frivolous, I think our *Journal* would be the better for an occasional "sweet disorder"—

> A careless shoe string in whose tie
> I see a wild civility
> Do more bewitch me than when art
> Is too precise in every part.

You have heard my opinion on the attempts at too profound a definition of colour. I have suggested that, although our *Journal* may not be written "for the few by the few"[29], much of the work published in it is read only by a few and understood by fewer. It is said that Great Britain lags behind in applied research[29]; briefly, we know "How" but we don't "Do".

In the first Mercer lecture[30] (here is a paper to read again and again) it was stated that "Technology to-day is the Cinderella of most Universities in this country". Who are the two ugly sisters? Let it never be said "The Society and its *Journal*"!

The history of our craft is literally full of colour, comedy, and tragedy. The *Journal* has printed throughout the years many fine historical publications, and the Society now has its Historical Records Committee, which augurs well for the future.

I have talked a little of the history of the *Journal*, and suggest that some of the old papers could be republished. I also ask the Society to foster talent for its *Journal*. It already has important rewards in medals and prestige; perhaps a different type of medal or prize competition will lure into print ungarnered aptitude and ability.

I am now in the throes of reading my December *Journal*— chastened, humbled, and with a sense of my own inadequacy. Like Job I say—

> WHO IS HE THAT HIDETH COUNSEL WITHOUT KNOWLEDGE? THEREFORE I HAVE UTTERED THAT I UNDERSTOOD NOT—THINGS TOO WONDERFUL FOR ME WHICH I KNEW NOT.

References

[1] J.S.D.C., **54**, 324 (1938).
[2] Neale, *ibid.*, **65**, 116 (1949).
[3] Callan, *ibid.*, **42**, 41 (1926).
[4] Hummel, *ibid.*, **1**, 11 (1884).
[5] *Ibid.*, **1**, 37 (1884).
[6] Bowman, **1**, 81 (1885).
[7] *Ibid.*, **56**, 265 (1940).
[8] Turner, *ibid.*, **65**, 49 (1949).
[9] Rowe, *ibid.*, **54**, 551 (1938).
[10] Walker, *ibid.*, **55**, 14 (1939).
[11] Saunders, *ibid.*, **60**, 81 (1944).
[12] Pennington, *ibid.*, **42**, 179 (1926).
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COMMUNICATION

Some Effects of the Evaporation of Water from Cotton Cellulose

W. A. Bone and H. A. Turner

Experiments with purified cellulose, air, and water indicate that an increased activity of the system is shown at the so-called "water-line". This is the narrow boundary region between wet and dry cloth which is formed when the lower end of a strip of bleached cotton fabric is dipped in water. Evidence is brought forward to show that the cotton cellulose is modified to give two distinct types of product— (a) one, soluble and transportable in water, brown in colour, markedly fluorescent in ultra-violet radiation, with enhanced reducing properties; (b) the other, solid, non-transportable in water, restricted to the boundary region, with higher cuprammonium fluidity and Methylene Blue absorption than the original cellulose. The action is not originated, nor does it seem to be greatly affected by light energy. Wide variations in the partial pressure of oxygen in the surrounding atmosphere cause little change in the apparent intensity of the brown line.

Introduction

GENERAL

A short account of this work was given some years ago by one of us (W.A.B.)[1]. From time to time there has been evidence of renewed interest in the subject, and it now seems that a more detailed account of the experimental methods and results would be of assistance to others who are investigating this and similar phenomena.

In 1929, Scholefield and Goodyear observed very marked differences, after exposure to light, between dry cloth dyed with an active vat dye and a similar dyed cloth exposed for the same time while saturated with water. The chemical modification suffered by the wet sample was much greater, as was the destruction of a direct cotton dye with which the vat dyeing had been topped. In an attempt to obtain a stricter basis of comparison, these workers arranged that a single sample of vat-dyed cloth should be exposed with one portion dry and another portion wet. This was achieved by dipping one end of the cloth, in the form of a long strip suspended vertically, into water. The water rose by capillary action and was simultaneously evaporated from the wet cloth, so that ultimately the height of the rise was determined by the rate of these two opposing processes. If the rate of evaporation were maintained almost constant, the level of the rise remained steady also. It was observed that the maximum decolorisation of the accompanying direct cotton dye occurred at the extreme edge of the wet region, in a narrow band which is henceforward to be called the *water-line*. In long exposures, maximum tendering of the cellulose also occurred in this region.

The experiments of Scholefield and Goodyear were repeated with dyeings of a number of active yellow and orange vat dyes, these being exposed as before to the light from the Fadeometer arc while the lower end dipped into water. After some hours, the following effects were noticed—

(1) The water-line took the form of an irregular narrow band, much browner in colour than the original dyeing.

(2) The cuprammonium fluidity of the water-line region was higher than that of either the fully wet or the fully dry portions.

(3) With shorter exposures, the presence of a water-line of distinctive properties could be shown very clearly because it was able to absorb Methylene Blue strongly.

Further experiments showed that the formation of the brown water-line with accompanying high Methylene Blue absorption could be obtained in the absence of any dye, the absence of light, and at the ordinary temperature of the laboratory. It was, however, formed more rapidly if the temperature were raised.

Experiments will be described in which progressively more thorough efforts were made to eliminate accidental impurities in the cotton, the air, or the water as possible causes of the effect. Acid impurities present in ordinary air, iron in the cloth and the water, non-cellulosic impurities of the cotton, and the presence and growth of bacteria were all shown to be extremely unlikely as causes of either the brown colour or the modification of the cellulose. The experimental arrangements were improved in order that the rate of evaporation of water from the wet region could be more accurately controlled. In this way it was possible to ensure that the position of the water-line remained unchanged for several hours. This led to a narrowing of the discoloured region, and a consequent intensification of the effects associated with its formation.

As the system is one in which there is convection of water through the wet portion during the whole period of the experiment, it is clear that substances capable of transport in water, whether they are originally present as impurities in the cloth or the water or are being formed from the wet cellulose during the course of the experiment, will be carried upward to the water-line and concentrated there as a "tide-mark". So also may any agents, e.g. acids, oxidising agents, originally present in air or water but capable of causing a pronounced modification in the cellulose as they are concentrated during the continued process of evaporation.

The repeated purification, mentioned above, caused no substantial diminution in the intensity, rate of formation, or distinctive properties of the brown line. A reasonably high degree of purity in both water and air in the system was capable of direct attainment. The apparatus was constructed of chemically resistant glass. The purification of cellulose was capable of less direct assessment, for "pure cellulose" is difficult to define. In addition, however, to repeated prior extractions with alkali, air-free water, organic solvents, etc., the carriage of water-transportable impurities by the liquid rising up the strip in the evaporation experiments

themselves and their deposition at the water-line were employed as a purifying process for cloth to be used in further evaporation experiments.

The fact that, after the first removal of the grosser amounts of impurities, no further stage of purification leads under comparable conditions to a diminution in the intensity of the brown line suggests that modification of the cellulose is accompanying the evaporation of water from it. The modification may be occurring in the whole of the wet region, the brown line representing a "tide-mark" or accumulation of decomposition products carried by the rising current of water. Alternatively, modification of the cellulose may be occurring specifically at the upper limit of the wet cellulose. No decisive conclusion has been reached, but the evidence tends to favour the latter possibility.

PROPERTIES OF THE MODIFIED MATERIAL

These may be summarised as follows—

AGGREGATE PROPERTIES OF WATER-LINE REGION — Yellowish brown, with enhanced fluorescence when viewed in ultra-violet radiation. Brown colour removed by extraction with hot water or ethyl alcohol, and fluorescence then diminished. Enhanced absorption of Methylene Blue. Enhanced reducing power as demonstrated by copper number and tests with Harrison's reagent (alkaline silver thiosulphate). Slightly higher cuprammonium fluidity than the rest of the cloth.

EXTRACT OF BROWN MATERIAL— Some fluorescence of aqueous or alcoholic extract. Tests for reducing properties inconclusive. No evidence of acid properties.

PROPERTIES OF CLOTH AFTER EXTRACTION OF BROWN COLOUR— Modification of cellulose at the water-line demonstrated by enhanced cuprammonium fluidity, Methylene Blue absorption, and copper number.

EFFECTS WITH SPECIAL REAGENTS

Enhanced chemical activity at the water-line was shown by colour changes in this region when each of the following reagents was added to the water which was evaporated through the cloth— ferric ferrocyanide, Indigosol O4B (DH), ammonium vanadate, cobalt naphthenate[2]. Addition of hydrogen peroxide caused enhanced tendering at the water-line. The possibility of bacterial attack was eliminated by addition of mercuric chloride to the water.

EFFECTS OF ACTIVE VAT DYES ON THE COTTON

When active vat dyes (i.e. those which accelerate tendering by light or oxidising agents) are present in the dyed state, the cuprammonium fluidity is generally greater at the water-line than in either the fully wet or the fully dry region. In the absence of light, however, the additional effect of the dye is in no case very great.

EFFECT OF VARIATION OF ATMOSPHERE

At this stage, complete removal of oxygen from the experimental system was not attempted. Little apparent difference was observed in the intensity and rate of formation of the brown line when evaporation took place in an atmosphere of (a) cylinder oxygen, (b) cylinder nitrogen.

Experimental

PRELIMINARY EXPERIMENTS WITH VAT-DYED COTTON

In these experiments, a fully bleached, medium-weight plain cloth was further purified by boiling for 4 hr. in a 1% solution of caustic soda under the surface of the liquid, washed thoroughly, soured in 0·5% hydrochloric acid, washed until free from acid, and dyed, by the normal method, with one of the selected vat dyes (5% dyeing). After dyeing, oxidising, and washing off thoroughly in water, the dyeings were dried at room temperature, and cut into strips about 2 in. wide. They were suspended in front of the enclosed arc of a Fadeometer, with the lower end dipping into tap-water in a porcelain dish. Losses by evaporation were made up at intervals by addition of fresh water. Exposure continued for a total time of 50 hr. The following changes were observed—

(a) DYEINGS OF CALEDON YELLOW G— A deep greenish-blue line was formed at the evaporation level, with a broader and less intense, irregular, greenish-coloured region higher up. The colour reverted more or less completely to the original colour of the dyeing when the strip was removed and kept for several hours in the dark.

(b) DYEINGS OF CIBANONE ORANGE R— These gave a sharp brownish-red line at the evaporation level, with a secondary irregular brown line about 1 cm. higher up.

(c) DYEINGS WITH OTHER VAT DYES— These showed an intense dark-coloured line of brownish hue, and a secondary, paler, irregular brown line higher up.

(d) UNDYED CLOTH— Here a primary and a secondary brown line were formed. It was considered that the secondary line resulted from a disturbance of the balance between capillary rise and evaporation of water when the experiment had to be stopped each night.

All the exposed strips, including the undyed one, when treated in the cold for 10 min. with a 0·1% solution of Methylene Blue to which a little acetic acid had been added, showed an intense blue line at the evaporation level, and a paler one, corresponding to the secondary brown line, above it.

In view of the specific action of light on dyeings of certain vat dyes, it was decided to examine the effect of evaporation alone. Experiments with the same series of dyeings were therefore carried out in a yarn-drying stove, in the dark, at a temperature of 58°c. for three days. Distilled water was used, the reservoir was covered to minimise contamination, and the water level in it was maintained constant. The colour changes previously described were again observed, although the line at the evaporation level was more intense, and the secondary coloration weaker. Enhanced Methylene Blue absorption by the coloured line was again exhibited. The results of cuprammonium fluidity determinations are given in Table I.

A similar series of experiments was performed in which evaporation took place at room temperature (about 20°c.) in the dark for six days. The same general appearances and Methylene Blue absorptions were again in evidence. The results of

cuprammonium fluidity determinations are included in Table I.

TABLE I
Cuprammonium Fluidities of Dyeings exposed in the Dark

Dyeing (5%)	58°C. for 3 days			Room Temp. for 6 days		
	Wet	Dry	Evaporation Level	Wet	Dry	Evaporation Level
White control ...	7·9	9·6	11·5	8·7	8·9	10·2
Anthra Yellow GC (IG)	11·2	10·9	12·8	10·4	9·2	9·5
Cibanone Orange R (Ciba)	11·7	10·6	12·2	—	—	—
Caledon Yellow G (ICI)	10·7	10·6	11·7	10·4	11·5	11·9
Indanthren Brilliant Orange R (IG) ...	10·3	11·7	11·5	8·9	9·6	13·0
Anthra Yellow GC (IG) + Ciba Blue 2B (Ciba) ...	10·7	8·9	11·5	9·1	10·3	10·3
Caledon Jade Green X (ICI)	8·4	8·9	11·1	9·7	10·1	10·5

IMPROVED APPARATUS FOR THE EVAPORATION EXPERIMENTS

· Air from a water injector was passed through two Drechsel bottles, 10 in. high, containing glass beads moistened with concentrated sulphuric acid, two soda-lime tubes, a bubbler containing water, a control valve, and a flow-meter, before being passed into the evaporation apparatus. This consisted of a large glass belljar, covered with black cloth and resting on a ground glass plate through which holes had been made to permit the entry of inlet and outlet air tubes and leads for the heater. The latter consisted of a 40-watt carbon-filament lamp covered with an inverted nickel beaker. The inlet tube for the air led almost to the top of the belljar; the exit tube projected a few millimetres above the base-plate. The heater was placed in the centre of the belljar, and the strips were hung round it, at equal radial distances, from a frame made of glass rods. The lower end of each strip of cloth dipped into a Petri dish containing distilled water, the level of which was maintained by an inverted glass cylinder, also filled with distilled water, and held with its rim just touching the surface of water in the dish. By occasional adjustments, the volume of air passing through the apparatus in a given time could be maintained almost constant, and the brown line then formed was only 2–3 mm. broad. In six hours a well marked coloration could be formed.

Cloth for these experiments was prepared by desizing a loom-state, medium-weight, plain-weave cloth with malt extract, washing repeatedly in distilled water, and then boiling for 7½ hr. in 1% caustic soda solution under a pressure of 20 lb./sq. in., again washing repeatedly in water until all the alkali had been removed, and drying. At this stage, the cloth had a cuprammonium fluidity of 4. Before use, a sample of this cloth was freed from much of the air it contained by boiling for 15 min. in boiled-out distilled water, and was then transferred at once to 1% caustic soda solution, which had been maintained at the boil for 30 min. previously, and boiled for 1 hr. It was then transferred to boiling boiled-out distilled water, and washed with several changes, avoiding contact with the air as much as possible. It was left in cold boiled-out distilled water to cool. Souring in cold 0·5% hydrochloric acid for 1 hr. followed, and

then further washing in distilled water until all the acid had been removed. Cloth so treated, when exposed in the evaporation apparatus, gave a strong brown line in 6 hr. The whole series of operations described above, with the exception of the pressure boil in caustic soda, was repeated twice more, without causing any diminution in brown line formation after 6 hr. evaporation. Purifying treatments identical with those described above, when alternated with prolonged extractions in cold acetone, brought no apparent change in the ability to form a brown line.

An experiment, which showed clearly that more than one type of modification contributes to the brown line effect, was carried out as follows—A piece of cloth was exposed to evaporation, as described above, for 6 hr. and a well defined brown line produced. Two inches of cloth was then cut from the bottom of the strip, which was replaced in the apparatus, and the experiment continued. After some hours, it was found that the brown line had moved up the strip a distance equal to the length of cloth removed, leaving only slight traces of colour at its first position. On immersion in Methylene Blue solution, two strong blue lines of about equal intensity were formed, one at the initial and one at the final brown line position.

QUALITATIVE EXAMINATION OF THE PROPERTIES OF THE BROWN LINE REGION

PRESENCE OF IRON— Small samples of an exposed strip were cut from the brown line region and from the adjacent wet and dry regions. Each was tested separately, under comparable conditions, with minimal quantities of N. potassium thiocyanate solution. No increased red coloration was found in the sample cut from the brown line, nor in the solution used to test it.

WAXY MATERIALS— An exposed sample was dyed in a dispersion of S.R.A. Red 10 (BrC), an acetate rayon dye sensitive to the presence of fatty and waxy materials. No increased staining was observed at the brown line.

SOLUBILITY— The brown coloration at the evaporation level is removed by boiling the exposed sample in water for a few minutes. It can also be removed with cold or warm ethyl alcohol. The solution is brown in colour, the intensity depending upon the volume used for extraction. It tends to deepen on continued boiling. A brown line produced upon a strip of cloth, which has then been dried at room temperature, will go much deeper in shade if the pattern is kept for 10 min. in an oven at 100°C.

FLUORESCENCE— A sample of cloth on which a brown line has been produced will show a bright fluorescence at the line when examined in ultraviolet radiation. The fluorescence disappears when the brown line is removed by extraction with water. The conditions under which fluorescent water-lines are formed have been examined in some detail. In many of these experiments, the brown lines were produced with highly purified materials in a special apparatus to be described later. In all the experiments, the fluorescence is most marked at the evaporation level, but the originally wet portion

is always slightly more fluorescent than the originally dry portion.

Apart from the fluorescence exhibited by a fully formed brown line, obtained after several hours of evaporation, enhanced local fluorescence can be seen as a tide-mark after very short periods of contact with water. For instance, if a strip of purified cloth is dipped at one end into water for about one minute, so that a rise of two inches occurs, and is then dried in an oven at 95°c., a distinct fluorescent line is observed at the edge of the originally wet portion. A more elaborate experiment is to produce a line as described above, then dip the dried pattern for a rather longer period so that the water rises a greater distance, dry as before, and examine in ultra-violet radiation. The original fluorescent line has disappeared, and is replaced by one at the new water level. If this experiment is repeated a number of times, always increasing the height of the rise in successive repetitions, it is found that the lines of each of the earlier stages have disappeared, and the only one present is that which has last been formed. On boiling the whole pattern in water, all the fluorescence is removed, but on immersing in dilute Methylene Blue solution and washing, a series of faint blue lines is observed, each corresponding to one of the water levels attained in the experiments.

Where the brown line has been removed by boiling in water or alcohol, a slight increase in the fluorescence of the extract can be detected if it is small in volume. It is obvious, therefore, that the fluorescence is given by some substance soluble in alcohol. If a sample of cloth is repeatedly extracted with alcohol before attempting to produce a line by dipping in water and drying, it will be found that the fluorescence then appears with undiminished intensity, so that the fluorescent substance appears to be *formed* by the evaporative process rather than to be *collected* by it. Cloth partly wetted and examined in the wet condition shows no sign of a fluorescent boundary between wet and dry areas. The action of heat, or at least the drying brought about by heat, appears to be necessary. Experiments in which the cloth was dried at room temperature in a desiccator were inconclusive, possibly because the wet area first enlarges and then diminishes during the drying, owing to insufficiently rapid evaporation of the water it contains.

Dipping in dilute solutions of hydrochloric or of sulphuric acid, followed by drying, leads to strong fluorescence over the whole of the wetted area, with no special increase in the boundary region. Dilute nitric acid does not bring about an increase in fluorescence. Dilute solutions of hydrogen peroxide, sodium hypochlorite, or caustic soda, applied locally and dried in, give boundary regions that are only a little more fluorescent than when pure water is used.

If a layer of a fluorescent mineral oil covers the surface of the water in which the cloth is dipped, the portion of cloth which has come into actual contact with the oil fluoresces strongly; then practically no effect is seen in the area up which the water itself rises, and the fluorescence at the boundary line is almost identical with that given

by water in the absence of oil. This suggests that the transport of an impurity, insoluble or not readily dispersible in water and external to the cellulose, is unlikely to be responsible for the fluorescence.

There appears to be a direct connection between the intensity of the brown line formed at an evaporation level and the intensity of the fluorescence. This applies not only for brown lines produced by varying periods of evaporation, but also when the brown coloration is intensified by the action of heat on the dry pattern.

ENHANCED METHYLENE BLUE ABSORPTION— The results of a great many experiments, performed with increasingly thorough precautions to obtain pure air, water, and cellulose, allow the generalisation to be made that *whenever a brown line has been formed there will be an enhanced Methylene Blue absorption, irrespective of whether or not the brown coloration is present when the dye solution is applied.* Thus, a brown line can be formed on a strip of cloth, removed by extraction with water, formed again after drying but at a different level, and again removed, and the process repeated indefinitely. At each brown line level that has existed in the full history of the cloth, a blue line will be formed by development with Methylene Blue solution. Similarly, a strip of cloth may be subjected to a long period of evaporation in the apparatus, the rate of evaporation being diminished at intervals so that the evaporation level rises in a series of steps. At the end of the experiment, the brown line is found only at the topmost evaporation level, but on development with Methylene Blue solution, blue lines are produced at all the intermediate levels as well.

The development was carried out by immersing the strip in a cold solution of the dye (1 g./litre) for 7 min., stirring at intervals. The strip was then removed, washed in several changes of distilled water, and dried. No quantitative determinations of the local dye absorption were made at the time, but by estimation it was considered that the intensity of the final blue coloration was roughly proportional to the original brown coloration at the evaporation level.

REDUCING PROPERTIES— In considering the results of tests which may demonstrate the presence of material with enhanced reducing properties, some distinction needs to be made between those reagents whose action depends on the reduction of a metallic ion to a lower valency or to the metal, and which therefore are generally unambiguous detectors of reduction, and those which, like permanganates, can also be reduced by interaction with an oxidising agent like hydrogen peroxide. As will be discussed later, the formation of hydrogen peroxide has been considered as a possible cause of the observed modification of the cellulose.

(a) *Harrison's Reagent*— This was prepared in the usual way by mixing, immediately before use, in the order given, equal volumes of solutions of sodium thiosulphate (40 g./litre), silver nitrate (10 g./litre), and sodium hydroxide (40 g./litre). The reagent was brought to 90°c., and the sample

immersed in it for 3 min. The latter was then removed, and washed first in sodium thiosulphate (20 g./litre) and then in water. A strong brownish-black coloration is produced at the brown line, with a faint pinkish-brown tint on the rest of the sample, unless this has received an inadequate initial purification, when the general tint may be stronger. This brown line reaction is observed whether the brown coloration produced by evaporation is still present or whether it has been first removed with water or alcohol. Like the Methylene Blue absorption, it is formed on a sample at any place where there has been a brown line.

(b) *Caledon Yellow G Test*— A similar test for local reducing properties is furnished by boiling the cloth for a few minutes in a dilute alkaline suspension of flavanthrone. Reduction and dyeing of the dye occurs at the brown line region. As the colour of the yellow dye is not very intense, the effect can best be shown, after washing the specimen free from unabsorbed dye, by treating with alkaline hydrosulphite, when the strongly coloured leuco compound is formed.

(c) *Copper Number*— This value was determined by the micromethod of Heyes[3], which requires 0·25 g. of the cotton sample. Values of copper numbers will be given later in an account of the results obtained with the most satisfactory apparatus for evaporation. In general, the copper numbers of both the dry portions and the brown line region are higher than those of the wet region, the brown line showing generally, though not invariably, the highest of all.

OXIDISING ACTIVITY IN THE BROWN LINE REGION

As will be discussed later, one means by which the modification of cellulose in the brown line region may possibly be effected is the concentration there of traces of hydrogen peroxide or other form of activated oxygen formed by the interaction of water and gaseous oxygen in the wet portions of the cloth. To detect this it is generally necessary that some reagent shall be included in the water which is evaporated through the cloth, with the possibility therefore of direct interaction between this reagent and the cellulose. The results need to be interpreted with some reserve.

STARCH IODIDE— The cloth sample was first impregnated with a dilute solution of starch and potassium iodide, dried uniformly, and then subjected to an evaporation experiment. Such a sample gave a strong brown line, but no blue coloration at any part. A brown line was therefore produced on a strip of unimpregnated cloth, which was then immersed at once in a starch–iodide solution acidified with acetic acid. The original wet portion of the cloth was tinted faintly blue as compared with the original dry portion, but there was no enhanced blue colour at the brown line. This may be interpreted either as evidence that no oxidising compound is formed during the evaporation, or that the compound is continually formed in traces and carried up to the evaporation level, where it interacts preferentially with the cellulose. Such behaviour of hydrogen peroxide on cellulose would be unusual.

FERRIC FERRICYANIDE— An evaporation experiment was carried out for 5 hr., using instead of water a solution containing potassium ferricyanide (0·3 g./litre) and ferric alum (0·5 g./litre). The portion immersed in and immediately above the solution was coloured an intense blue, while a blue scum covered the surface of the solution. The colour diminished progressively in passing upward from the immersed portion of the cloth, until the topmost part of the wet region was colourless for a distance of 1–2 in. The blue colour then appeared strongly at the evaporation level. Thus there seemed to be a general decomposition of the reagent in the solution, the cause for which was not clear. This seems to produce a pigment which is filtered out by the cloth as the solution ascends. This decomposition may be incomplete, so that some reagent succeeds in reaching the evaporation level, where it is changed, either specifically by active substances formed or collected there, or by the cellulose that has undergone prior modification as a result of the evaporation of the water alone. The blue coloration suggests reduction, but interaction of ferric ferricyanide with hydrogen peroxide also causes the formation of a blue colour.

DECOMPOSITION OF INDIGOSOL SOLUTIONS— A solution containing 0·015 g./litre of Indigosol O4B (sodium sulphuric ester of reduced tetrabromo-indigo) was used in evaporation experiments. At the end of 6 hr. the solution was undecomposed, and the wet portion of the strip was uncoloured, but a strong blue line formed at the evaporation level. Similar results were obtained by longer periods of evaporation at room temperature. In none of these experiments was access of light allowed. Two main possibilities may be considered in attempting to explain this action, and one does not exclude the other. The first is that hydrolysis of the Indigosol is being encouraged by the special conditions which obtain at the evaporation level, e.g. local concentration of acid, differential absorption of ions by the cellulose, etc., so that formation of the free leuco compound results, and this is then oxidised by contact with the air. Development of the vat dye by hydrolysis and air oxidation does not seem to be a characteristic behaviour of the Indigosols. The second possibility is that an active oxidising agent is being formed or is being concentrated at the evaporation level.

With both Indigosol solutions and ferric ferricyanide reagent, capillary rise experiments were carried out through strips of porous tile, representing a substrate more inert chemically than cellulose. These did not reproduce the coloration at the evaporation level observed with cellulose. The colour was developed low down the strip, contiguous to the solution, so that it is very probable that the reagents are affected by chromatographic phenomena, i.e. specific and differential absorptions of the constituents of the solution on either the cellulose or the porcelain.

AMMONIUM VANADATE— A solution containing 0·5 g./litre of ammonium vanadate was evaporated through the cloth for a total of 6 hr. At the end of 1 hr., a yellow–orange line appeared at the evaporation level. In 6 hr. the colour of the line had

changed to bluish green, which appeared, therefore, to correspond to local reduction of the vanadate.

COBALT NAPHTHENATE — Charitschow[2] states that one part of hydrogen peroxide in 10^6 parts of water can be detected by the colour change produced in paper impregnated with cobalt naphthenate. He found that the paper reacted when placed in contact with moist porous substances such as wood, asbestos, pumice, etc., and also when brought into contact with the surface of water which had been exposed to bright sunlight. A number of evaporation tests were carried out with cloth which had been impregnated with this reagent from solution in petroleum ether. The results were inconclusive. A series of broad fringes, ranging in colour from yellow through brown to pink, were formed near the evaporation level, but additions of hydrogen peroxide to the water before the evaporation did not cause any marked difference in the final results.

ADDITION OF OTHER REAGENTS TO THE WATER USED FOR EVAPORATION— These reagents were added, not as detecting substances, but as substances that might accelerate or inhibit local oxidation at the evaporation level. The solutions were—(a) distilled water (control), (b) 0·1-volume hydrogen peroxide, (c) tannic acid (1 g./litre), and (d) 0·01 N. caustic soda. Exposures were carried out at room temperature for one week. In all cases a brown line was formed; it was very strongly coloured with the tannic acid solution. Microdeterminations of cuprammonium fluidity were made on cloth from the wet, dry, and evaporation-level regions. The determination is described later in this paper (p. 323). Results are given in Table II.

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TABLE II

Cuprammonium Fluidities of Cotton dipping into Various Reagents

(Original fluidity 4·4)
</div>

Reagent			Wet	Dry	Evaporation Level
Water	...	...	6·0	4·9	5·8
Hydrogen peroxide ...		...	6·3	5·1	13·0
Tannic acid (1 g./litre)		...	5·5	4·7	4·8
Caustic soda (0·01 N.)		...	6·6	4·2	7·2

Hydrogen peroxide and caustic soda are the only members of this series which might be expected to cause increased modification of the cellulose, the former by direct oxidative attack, the latter by acceleration of the normal slow oxidation of cellulose by atmospheric oxygen. It is interesting, in the experiment with hydrogen peroxide, to see how the amount of peroxide which must be continually present in the solution which saturates the wet region has been able to cause a fluidity rise of only about 2 in six days, while at the evaporation level a rise of about 9 has taken place. This may also be taken as an illustration of the way in which a chemically active substance, produced in very small quantities in the wet region, and concentrated by evaporative action at the water level, would then be able to cause greatly increased modification of the cellulose.

DISTINCTION BETWEEN OXIDISING AND REDUCING ACTIONS AT THE EVAPORATION LEVEL

In dealing with the possible modification of cellulose by an active oxidising agent which is

formed continually during the evaporation, and which exerts its greatest effect at the evaporation level, a clear distinction should be drawn between the interpretation of tests for oxidising action and tests for reducing action. The second-named may respond to, inter alia, the presence of an oxidised or of a hydrolysed cellulose of aldehydic properties, or to an oxidising agent of the peroxide type. The first-named should not be able to detect any action in which the cellulose or its modified forms would normally take part, but should be sensitive to an active oxidising substance produced externally to the cellulose. On bringing together the evidence just set out, it seems that reducing modifications of the cellulose are formed, and perhaps also collected, at the evaporation level, but that some at least of the reducing substance is not transportable in water. It suggests, further, that carboxycellulose is formed also at the evaporation level, and that this is for the most part not transportable. Hydrogen peroxide may be formed in the wet cloth and collected at the evaporation level, but the evidence is not conclusive.

In an attempt to assess the relative parts played by oxidising and reducing actions in this phenomenon, dilute solutions of Methylene Blue, which is reduced to a practically colourless leuco compound, and of Brilliant Green YS, which is readily decolorised by many oxidising agents, were evaporated in the usual manner through strips of cloth. With both a phenomenon occurred which has been observed with a variety of soluble dyes. With Methylene Blue, the dye was carried up the strip to within an inch of the evaporation level, then a space free from colour was left, and finally a deep chocolate-brown line at the evaporation level. This line could be formed by the shading of a normal brown line with blue. With Brilliant Green YS, the cloth was also dyed for some distance along the wet region contiguous to the solution, then there was a clear space, and then an intense green line at the evaporation level. If the experiment with either dye were continued long enough, the colour gradually rose up the strip, until there was no colourless interval between the solution and the evaporation line. The portions coloured with Brilliant Green YS were found to be dyed with remarkable fastness; soaping the specimen at the boil did not remove the dye. It appeared, therefore, that an association between dye and the cellulose, probably due to the presence of carboxyl groups, had occurred. There was no change in the colour of the respective dyes to suggest that oxidation or reduction had taken place. The appearance observed in the first stages of the evaporation could be accounted for by supposing that practically all the dye was absorbed by the lower portion of the strip from the rising solution, allowing a solution to go forward that was so dilute as to be imperceptibly coloured. The dye in this solution would become concentrated at the water level in the course of time, building up a visible coloured line.

POSSIBILITY OF THE CONCENTRATION OF ACID AT THE EVAPORATION LEVEL

Evaporation of dilute solutions of B.D.H. Universal Indicator through a fully purified strip

of cloth gave a red line at the evaporation level, corresponding approximately to pH 4. In time also the water in the reservoir changed from its original value of pH 6 to pH 4. These values were obtained on a number of occasions with cloth that had received a variety of purification treatments, including some specimens that had been boiled several times in alkali but had suffered no contact with acid. Evidence obtained by the application of indicators, and especially mixed indicators, to cloth is not always capable of simple interpretation, but with this reservation, it may be thought that the present results show that the evaporation system is a powerful device for building up appreciable local concentrations of acid at the evaporation line from minute traces of acidic impurity introduced with, say, the air passing through the system. An equally probable explanation would be that a cation interchange may occur between newly formed carboxyl groups at the evaporation level and the salts of the indicator acids.

EFFECTS OF ALTERATION IN THE COMPOSITION OF THE ATMOSPHERE

If the oxygen of the air does play a part in the modification of the cellulose, at the evaporation level or elsewhere, it is to be expected that, complete exclusion of oxygen from the system apart, the effect might be enhanced and accelerated by evaporating in an atmosphere consisting almost entirely of oxygen, and inhibited or retarded in an atmosphere consisting almost entirely of nitrogen. To test this supposition an apparatus was constructed in which a Liebig condenser was fixed vertically with the lower end of the inner tube passing through a soft rubber stopper fitting in the neck of a 150-c.c. extraction flask. Gas was passed into the top of the condenser tube, and after flowing down through the system, escaped through an exit tube in the stopper of the flask. A narrow strip of cloth was suspended within the inner tube of the condenser with its lower end dipping into distilled water contained in the flask. Care was taken to avoid contact between the cloth and the walls of the tube. An arrangement was provided for lifting the strip up and down without opening the apparatus. The water in the flask was boiled *in situ* for 30 min. before commencing the experiment.

Ordinary cylinder nitrogen was passed through a bubbler of concentrated sulphuric acid, two soda-lime towers, and two Drechsel bottles containing alkaline pyrogallol before entering the apparatus. The apparatus was set up, the water boiled, steam passed through the jacket, and nitrogen passed through the inner tube and flask for 1 hr. The stream of gas was maintained and the cloth strip lowered to make contact with the water. Evaporation was continued thus for 30 hr. without interruption, at the end of which time a well marked brown line was formed, with the usual enhanced absorption of Methylene Blue.

The experiment was repeated, the nitrogen being replaced by cylinder oxygen which had passed through the sulphuric acid bubbler and the two soda-lime towers. Brown line formation and Methylene Blue absorption did not appear to be greater than with the nitrogen atmosphere. The strip was

too narrow to allow fluidity or copper number determinations to be made. These experiments may be taken to indicate that oxygen plays no part in the modification of the cellulose or that very small quantities, previously occluded in the cellulose, and not removable by the above treatment with nitrogen, are sufficient to give the effect. Experiments based on the same principles as the above, but in which the difficult task is undertaken of decreasing the oxygen contents of cellulose, water, and atmosphere to very low values may prove to be crucial in obtaining a satisfactory explanation of the brown line effect. An investigation on these lines has now begun.

FINAL FORM OF THE EVAPORATION APPARATUS

With the exception of a few interpolations of results obtained with the apparatus now to be described, most of the evidence set out above has been obtained in the belljar apparatus, and has served to give a general insight into the formation and properties of the brown line. Based on experience with the condenser apparatus, a new equipment was designed, in which more thorough purification of the air was attempted, and in which the evaporation could be performed in a closed system consisting entirely of glass. The volume of the apparatus compared with the size of the cloth sample was also much smaller, so that sweeping out with the purified air was more efficient. It is described as follows—

AIR-PURIFICATION TRAIN— Air, from a small, slow-speed, electrically driven, piston pump, in excess of that required for the evaporation, was passed into a container with a blow-off valve set to operate at 15 lb./sq. in. excess pressure, and thence through a needle valve and Venturi flow-meter to the purification train. The pump was run during the whole time of the experiment, and occasional adjustment of the valve served to maintain a steady flow of air. At this time the electric supply was interrupted during the night, and the consequent disturbance of the rate of evaporation made it impossible to work for periods longer than about 8 or 9 hr. It was found more convenient to accumulate the amount of modified cellulose necessary for testing by exposing a fresh strip each day. The position of the evaporation level was almost entirely dependent on the rate of flow of the air through the apparatus. The purification train is described in Table III, which gives the order and functions of the constituent units.

TABLE III
Purification Train

Purification Units (Pump, reservoir, valve, flow-meter)		Designed to remove
...	...	—
1 wash-bottle* 10% KI	...	H_2O_2, O_3, N_2O, etc., Cl_2
1 wash-bottle 0·2N-$KMnO_4$	...	H_2O_2, N_2O, SO_2
1 wash-bottle 25% H_2SO_4	...	NH_3
1 wash-bottle conc. H_2SO_4	...	SO_2, NH_3, organic matter
2 wash bottles 25% NaOH	...	SO_2, SO_3, other acid gases
2 towers anhyd. $CaCl_2$	...	Moisture
1 tower solid KOH	...	Moisture, acid gases, spray
1 long tube, glass wool	...	Dust, spray

* The wash-bottles consisted of 10-in. Drechsel bottles containing glass beads.

Air passed through the above train was bubbled for 5 hr. into distilled water in a glass cylinder.

The water then had no effect upon a very dilute solution of potassium permanganate, but caused slight greening of a ferric ferricyanide solution. The pH had changed from 6 to 8. On repeating the experiment, using boiled-out, distilled water in a well steamed silica flask, no change in either reagent could be detected, and the pH had not changed. Air from this train, passed directly into 0·001 N. permanganate in a silica flask for 2½ hr., caused no change in the colour as measured in the Leitz colorimeter. With dilute ferric ferricyanide, passage of air for 2½ hr. caused no development of a green or blue colour, but a slight cloudiness was observed.
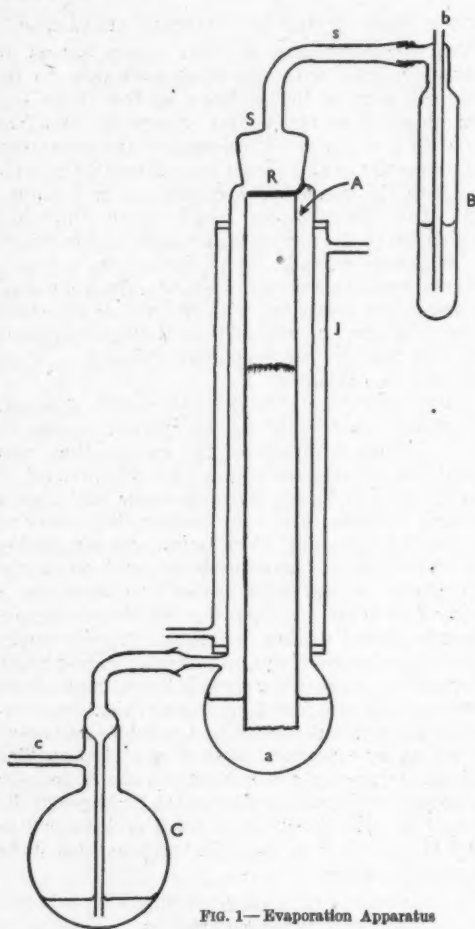

FIG. 1—Evaporation Apparatus

EVAPORATION APPARATUS — This was made entirely in Pyrex glass, and was designed to avoid the contact of water, cotton, or moist purified air with rubber or other organic materials. Before the actual evaporation commenced, purified air could be circulated through the water to be used and over the strip of cloth. The apparatus consisted of the evaporation cylinder A (Fig. 1), with a bulb a at the bottom to hold the supply of water for evaporation. It was heated externally by the steam jacket J, and connected through ground joints to the flask C and

outlet c. The top of A was closed with a ground-in stopper S, bearing a horizontal rod R to which the strip could be attached. S was connected through the inlet tube s by a ground joint to bubbler B and inlet tube b.

METHOD OF USE— The strip was suspended from R and made long enough to reach within 1 cm. of the bottom of a. Care was taken in the cutting and attachment of the strip to make sure that it would hang straight and not touch the sides of A. A little more water than would be needed in a was placed in C (distilled water or, in later experiments, conductivity water). Steam was circulated through J, and B was surrounded with a mixture of ice and salt. The supply of purified air was connected with b, and passed through B, over the strip in A, and bubbled through the water in C, which could, if required, be boiled while the bubbling continued. This operation continued for 30 min., after which the air supply to b was disconnected and attached to c. The pressure of this air forced the water over from C to a, and evaporation commenced. The evaporated water condensed in B and thus formed a trap against the entry of the outside air. As mentioned above, the position of the evaporation level depended entirely on the rate of air flow, and was not affected by the slight fall in water level in a as evaporation proceeded.

PURIFICATION OF THE CLOTH— This can be described in synoptic form—

(1) Medium plain grey cotton cloth singed, desized, washed, kier-boiled at 20 lb./sq. in. for 7 hr., washed until free from alkali, and dried. This was the basic material, from which convenient small quantities were further purified from time to time as required. Cuprammonium fluidity 4.

(2) Boiled for 15 min. in boiled-out distilled water, transferred at once to next stage.

(3) Boiled for 2 hr. after entering into boiled-out, boiling caustic soda solution (1% AnalaR reagent in distilled water). Transferred at once to next stage.

(4) Entered below the surface of boiling, boiled-out distilled water, and allowed to cool.

(5) Washed with three changes of cold distilled water.

(6) Soured for 30 min. in hydrochloric acid (0·5% pure HCl in distilled water).

(7) Washed in at least seven changes of cold distilled water, until washings free from acid.

(8) Dried.

(9)–(11) Sequence of operations (2)–(8) carried out three more times; at the fourth boiling in caustic soda solution only slight yellowing of solution observed. Fluidity 5·6.

(12) Extracted for 5 hr. in pure, redistilled chloroform in Soxhlet. Fluidity 5·9.

(13) Extracted for 4 hr. with absolute alcohol in Soxhlet. Fluidity 5·3; copper number 0·02.

EXAMPLES OF RESULTS OBTAINED— A sample of the purified cellulose was exposed in the apparatus for 19 hr., using conductivity water. A narrow, strongly coloured brown line resulted. Enhanced Methylene Blue absorption at the line was obtained. A similar strip, after one day in the

apparatus (7 hr.), gave a black line at the evaporation level when tested with Harrison's solution. The water which condensed in the receiver B at the end of this run had slightly increased in alkalinity as compared with the original conductivity water, i.e. from pH 7·5 to pH 8. The condensate gave slight greening when added to dilute ferric ferricyanide solution, but had no effect on very dilute permanganate.

It has been pointed out that it was normally impossible to keep the evaporation level constant, and the brown line restricted in width, for periods of operation over one day. An evaporation period of this length did not suffice to produce really marked changes in the cuprammonium fluidity. Running for longer times and tolerating more diffuse evaporation-level regions did not solve this difficulty, since such modified cellulose as may have been formed was associated with a greater weight of unmodified material. Working for one day with very careful control of the air current so as to obtain narrow and intense lines, and using a small-scale version of the normal Shirley viscometer (described in the next section), which required little more cloth for a sample than corresponded to the brown line, did not give decisive results. It was decided, therefore, that the copper number might prove to be a more satisfactory measure of degradation, since, providing the copper number of the original cloth were low, it would not matter, within fairly wide limits, how much unmodified cellulose were associated with a satisfactory quantity of modified material. In this way it was possible to run several evaporation experiments on successive days and to cut out the brown line from each exposed strip until a satisfactory quantity of reducing substance had been accumulated to give a marked rise in copper number as compared with similar accumulations of material, of the same weight, cut from the corresponding wet and the corresponding dry regions.

As an example of such values may be cited a series of experimental results obtained in an investigation of the effect of light during the evaporation (Table IV). The total evaporation time in each series was 19 hr. over three days, using three separate strips. One series of evaporations took place in complete darkness, the other during summer time in bright daylight indoors.

TABLE IV
Effect of Light on Copper Numbers
(Original copper number of cloth 0·02)

Series		Wet Region	Dry Region	Evaporation Line
Dark	...	0·03	0·09	0·16
Light	...	0·06	0·13	0·18

The above determinations were made upon the strips just as they were removed from the apparatus, with no further treatment except drying, the brown substance therefore remaining on the cloth. It had previously been shown that the soluble brown substance possessed reducing properties, and it was desired to see how far the residual modified material which survived extraction was responsible for the total copper number. Table V gives results of evaporation on three successive days with three separate strips in each series. In one series, the

strips were taken from the apparatus and dried without further treatment, and the requisite samples cut from them. In the other, after the strips had been removed from the apparatus they were boiled for one hour in distilled water, all trace of the brown colour being removed, and then dried and used for the determinations. Repeat results are given in Table V.

TABLE V
Effect of Extraction with Boiling Water on Copper Numbers
(Original copper number of cloth 0·02)

		Wet Region	Dry Region	Evaporation Line
Unboiled strips	...	0·02	0·03	0·05
Boiled strips	...	0·02	0·02	0·03
Unboiled strips	...	0·02	0·05	0·07
Boiled strips	...	0·02	0·04	0·05

These values, taken with the series in Table IV, although corresponding to very small differences, are consistently higher at the evaporation level than in the other portions of the cloth. It is interesting to find that the copper number of the dry portion seems always to be higher than that of the wet portion. This may be explained by supposing that all the cloth, wet and dry, when exposed to a current of heated air in the apparatus, is modified to approximately the same extent, and corresponding to a rise of copper number equal to that observed in the dry portion. In the wet portion, however, the rising current of water transports some of the modified material and deposits it at the brown line. This hypothesis will be discussed later.

MODIFIED CUPRAMMONIUM FLUIDITY DETERMINATION— In the earlier experiments, where normal cuprammonium fluidity determinations were made on various portions of cloth strips used in evaporation experiments, the method used was that described by Clibbens and Geake[4]. This method requires about 0·1 g. of cotton for each determination, and this corresponds to a much greater area of cloth than is covered by a satisfactorily concentrated evaporation line. Samples taken from the region of this line must of necessity include cloth which belongs strictly to the adjacent regions, where less modification is indicated by other tests, and the fluidity test loses much of its discriminating power. A viscometer of the straight-tube, open-jet type, similar in shape to the standard viscometer used by the above workers but reduced in size, was constructed. The principal dimensions were as follows—

Main tube	9 cm. long, 7 mm. internal diameter
Jet	2 cm. long, 0·8 mm. internal diameter
Distance of etched rings on main tube from mouth...	0·4, 1·4, 4·4, and 7·4 cm.

The jet was closed by a cap made from a short length of pressure tubing, in one end of which a plug of solid rubber was inserted. The top of the viscometer was closed with a stopper made from pressure tubing and inserted to the level of the first ring. Through this stopper passed a short length of quill tubing, the lower end of which was flush with the inner end of the stopper, the upper end carrying a short piece of small-diameter rubber tubing closed by a small ($\frac{1}{4}$ in.) screw-clip. The stirrer was 0·2 c.c. of mercury. The instrument was used exactly as the full-size viscometer, except that

it was calibrated with a standard cotton, whose fluidity had been determined with a large viscometer. The accuracy to be attained with the small-size instrument is illustrated by the results in Table VI, all of determinations on the same sample of cotton.

TABLE VI
Accuracy of Small Viscometer
(Value by standard method 4·55)

Viscometer No.	Determination	
	First	Repeat
1	4·45	4·36
2	4·41	4·45
3	4·75	4·75
4	4·40	4·48

EVAPORATION UNDER DELIBERATELY STERILE CONDITIONS— The conditions at the lower end of the cloth strip in all the evaporation experiments where the cloth is saturated with water, and in some where it is also warm, are generally favourable to the growth of micro-organisms. If these organisms can live and multiply, then the brown line may consist either of the accumulated organisms themselves, of cultures which find themselves encouraged in growth by the special conditions of the evaporation line, or of modifications of cellulose produced by biological action. As the purification of the cloth, the air, and the water becomes increasingly thorough, it becomes more difficult to understand either how infection can occur, or how the organisms can find the necessary food. Apart from the steps taken to purify the components of the system, no deliberate measures of sterilisation had been undertaken, and therefore experiments were carried out in the improved apparatus in the presence of an antiseptic. The strip of cloth was heated for 20 min. to just below the boil in a solution containing 0·1 g. of mercuric chloride per litre. It was then transferred to the evaporation apparatus, suspended in the tube A, and dried in position with the air current and the steam jacket in action, but with the lower end withheld from contact with water. When dry, water containing 0·1 g. of mercuric chloride per litre was forced over into the bulb a, and used for the evaporation. At the end of 6 hr. a brown line of normal intensity was formed, exhibiting the usual properties of enhanced fluorescence and Methylene Blue absorption. Biological growths seem, therefore, to be excluded as causes of the effect.

Discussion

GENERAL

Whatever the ultimate explanation of the formation of the brown line, there can be little doubt that it indicates at least the continuous modification, chemical or physical, of fibrous cellulosic structures exposed to the air. The investigation of this effect should therefore be of interest in studies of the deterioration of cellulosic materials during weathering. The special effects that are observed when part of the area is wet and part is dry should have a practical significance in the investigation of the behaviour of natural, and probably also regenerated, cellulosic materials in situations where cloth is intermittently wetted and dried, e.g. in awnings, sails, curtains, etc. During discussions it has also been suggested that the staining and

irregular dyeing properties, sometimes encountered when piles of wet cloth and bundles of wet yarn are allowed to stand and to dry on the surface of the mass, are connected with the brown line phenomenon. Such deductions, when they have to do with specific practical examples, should be made with great caution, since there are likely to be factors, e.g. sunlight or the presence of natural non-cellulosic impurities, of finishing agents, and of micro-organisms, which the present experiments have attempted to exclude. There is little doubt that, when the evaporation conditions are so adjusted that the boundary between the wet and the dry regions remains practically stationary, a powerful means exists for concentrating traces of mobile impurity distributed through the wet area into a very much more restricted area, and so of demonstrating their presence very effectively. A mechanism of this kind is not unexpected. A less usual feature of the present work is constituted by the indication that chemical modification of the fibre substance may be markedly different in degree, and perhaps also in kind, in the boundary area as compared with the rest of the cloth.

Indications of this kind do not seem to have been described before, and it has been stressed already that rigid proof of specific chemical effects in the boundary region calls for an experimental technique of great refinement. Assuming, however, that the indications can be interpreted in this sense— and the strongest evidence in support is the high local absorption of Methylene Blue, not substantially diminished or moved in position by previous extraction with water or alcohol— then two types of formative mechanism require to be discussed—

(a) The presence or formation within the whole of the wet region of a chemical, e.g. hydrolytic or oxidising, agent, which is collected at the boundary in such concentrations as to cause detectable changes in the cellulose.

(b) The modification of the cellulose in the boundary region by influences which do not exist at all in other parts of the cloth.

Before considering these possibilities critically, mention should be made of some of the chemical relations between cellulose and (i) water, (ii) air or atmospheric oxygen.

CHEMICAL RELATIONS BETWEEN CELLULOSE AND WATER

The literature of the subject is extremely voluminous, and it is beyond the purpose of this paper to give a review. It can be said briefly that the experimental evidence of a direct chemical combination between water molecules and the hydroxyl groups of cellulose rests for the most part upon studies of the absorption and desorption of water by the cellulose which occur when the external concentration of water is varied, and upon the dimensional changes which accompany these processes. Useful summaries are given by Valko[5] and by Hermans[6]. Evidence of the existence of chemical bonds is furnished by the great difficulty of removing all traces of water from cellulose, by the positive heat of wetting, and by the hysteresis

found to occur in absorption–desorption cycles. The normal criterion of chemical combination for simpler substances, viz. the formation of compounds of fixed composition, is not applicable, because the very complex and imperfectly stable structure of fibrous cellulose does not permit a complete or constant access of water molecules to all the points in the constituent molecules which are potentially capable of interaction. Fibrous cellulose, consisting of molecules bonded together at many points along their length, can be swollen but not dissolved by water, whereas an isolated cellulose molecule, especially in the extended form, should be very soluble. It may be imagined, therefore, that fibrous cellulose does contain a few molecules, capable of such isolation, which could be transported in water, and concentrated from a wet region to its boundary. If such isolated molecules can be obtained readily from, or exist in, native cellulose, it is unlikely that they would survive the thorough purification which has been given to the cotton samples in this work. Most of those which may exist during the course of the evaporation experiments are likely to have been separated by the action of the water then present. They might be considered as the representatives of a process of molecular separation carried to its extreme, the majority of the cellulose molecules being separated incompletely, and to an extent corresponding statistically to the volume swelling. This isolation of cellulose molecules as single units or as very small groups could be assisted if some depolymerisation had taken place. When separated and in the course of transport, such molecules would be expected to be specifically more reactive than the rest and to be prone to further chemical modification. A molecule once separated from association with others, i.e. dissolved, should become less liable to be re-attached to the solid material if it remains free long enough to crumple and to allow some cross-linking to occur between the hydroxyls along its length.

The solution of cellulose in the manner just discussed does not appear greatly to have interested workers who have studied fibrous cellulose in textile products, but it has been put forward, with some formal elaborations, by paper chemists, who deal with heavily fibrillated cellulose, and who produce the fibrillation by maceration during long periods of contact with water. The concept of "heavy hydration" or "partial solubility" has been used in different ways by Schwalbe[7], Campbell[8], and others to provide a hypothetical bonding agent, in the more extreme views a mucilage, of disoriented cellulose molecules by which the fibrillated surfaces of the paper fibres are held together. The presence of this material is held to be largely responsible for the strength of the dry sheet, and its ready dispersibility for loss of strength on wetting. Strachan[9], initially an opponent of this theory, has described the continuous removal of traces of organic substance, with marked reducing properties, during the repeated extraction of purified cellulose with cold water. Further speculations upon the cause of the adhesion of the constituent fibres of paper are given by Clark[10].

Other evidence of the gradual modification of cellulose by water, under comparatively mild conditions, is given by Heubner and Kaye[11]. They state that distilled water in which purified cellulose had been soaked for several days at 35°C. gave a mirror with ammoniacal silver nitrate and a coloration with Schiff's reagent. The reducing substance proved to be volatile in steam. Positive reactions for aldehydes were given by water kept for several days in a closed container in which bleached cotton had been present out of contact with the water. Erban[12] gives examples of the browning which takes place in damp, bleached goods allowed to stand overnight under conditions which encourage local evaporation, but is more concerned to show that this may be connected with the presence of impurities than with an attack on the cellulose itself. It seems to be an established fact that carefully bleached cotton will go brown on prolonged steaming, and that marked amounts of decomposition products are not obtained until the steam temperature reaches about 140°C.

CHEMICAL RELATIONS BETWEEN CELLULOSE AND ATMOSPHERIC OXYGEN

It is generally accepted that the gradual deterioration of fabrics exposed to the air is, in part at least, due to oxidation of the cellulose, but the influence of other factors, e.g. light, moisture, atmospheric contaminants especially mineral acids, or the presence of specific dyes and finishing agents may be very considerable, and not always easy to define quantitatively. With the exception of studies of the effect of air on alkali cellulose[13] in the ageing process, little work has been done on the degradation by gaseous oxygen of cellulose which has been exhaustively purified. Scheurer[14] states that, below 150°C., water does not appreciably affect the strength of unbleached cotton, but that prolonged treatment with steam containing air results in a loss of tensile strength approximately proportional to the time of treatment. Knecht[15] heated cotton at 90°C. (i) with free access of air, (ii) in sealed tubes with the cotton containing approximately its normal amount of moisture before introduction into the tube, (iii) in evacuated sealed tubes. Both grey and bleached cotton were investigated. In every case a reduction in strength and a rise in copper number were observed. The cotton in (i) showed the greatest loss in strength. The air of the tube in (ii) contained a volatile acid at the end of the experiment, and a partial vacuum had been formed, suggesting some consumption of oxygen. Loss in strength was least in (iii), but a marked browning was observed. Wiegerink[16] showed that percentage loss in both strength and extension, as well as rise in fluidity, increases with increasing temperature when fabrics are dried at 105–149°C. The changes are greater with high than with low initial moisture contents for bleached cotton and for cuprammonium rayon, but moisture has much less effect with viscose and with mercerised cotton. The information available, therefore, though not presented in a strictly quantitative form, is sufficient to show that gaseous oxygen will react with cellulose, slowly at low temperatures, more rapidly at high, with the usual concomitant of

oxidation, viz. discoloration, which is generally the first evidence to be recognised, followed by loss in tensile strength, rise in copper number and cuprammonium fluidity, and evolution of volatile acidic products.

OXIDATION BY ACTIVE FORMS OF OXYGEN

The exclusion of light, and the passage of the air through reagents which should remove ozone, peroxides, and other active oxidising substances formed directly from atmospheric oxygen, would seem to limit the production of these substances except in very small amounts, unless it can be shown that they are formed either by simple contact between air and water, or else during the evaporation of water into air. If either of these actions is possible, then the increase of the water–air interface, resulting from the distribution of the water in thin films in the wet cloth, should encourage the formation of the active product. Dixon[17] claimed to have demonstrated the formation of hydrogen peroxide when pure water was evaporated in a porcelain dish over hot sand, i.e. away from the vicinity of flames or the surfaces of very hot metals. He failed to confirm it in later experiments, and we ourselves have not been able to find conclusive evidence of peroxide formation under the conditions which he employed. Ramsay[18] found that distilled water had a decolorising action on potassium permanganate, and this he considered too great to be accounted for by any expected or demonstrated contamination. Smith[19] studied the evaporation of water over an extremely wide range of conditions, and failed to find any evidence of peroxide formation, with the single exception of evaporation from zinc containers. As previously mentioned, Charitschow[2] claimed that he could demonstrate the presence of traces of peroxide on a number of moist, porous solids, by means of cobalt naphthenate paper.

POSSIBLE CAUSES OF THE BROWN LINE EFFECT

In the earlier parts of this paper, a number of alternative actions have been mentioned. These alternatives include—(1) a restricted dispersion of free or slightly aggregated cellulose molecules by water, and their transfer by convection to the boundary region; (2) modification of cellulose over the whole area of the test strip, and the collection of the modification product occurring in the wet part by convection at the boundary line; (3) modification by water, or by water and air, in the wet region only, and transport of the modified product to the boundary line; (4) initial presence, or formation during the experiment, in the wet area, of a substance capable of reacting with cellulose, and the concentration of much of this substance at the boundary line before it has been able to react with the cellulose in the wet region generally; (5) a specific change in the cellulose which can take place in conditions which exist in the boundary region, and nowhere else.

If the soluble, brown, fluorescent substance were the only recognisable modification of the cellulose produced during evaporation, then all of these alternatives might find some *a priori* justification.

The presence of a non-dispersible and non-transportable modification at every position in the cloth where a boundary between wet and dry has existed for an appreciable time reduces the probability of the alternatives (1), (2), and (3). The simultaneous evidence of reducing and of acidic properties in the non-mobile modification supports the view that it is most likely to be an oxidised form of cellulose. If decisive evidence of the formation of a peroxide, or similar active form of oxygen, through simple evaporation of water into air from a cellulose surface could be obtained, both alternatives (4) and (5) would be favoured. The activation of water molecules by evaporation alone is not easy to understand, for although the molecules which do escape from the surface must have an energy content beyond the average, this energy is largely expended in effecting an escape.

If, therefore, alternative (5) is considered alone, it is necessary to attempt a definition of the uniquely favourable conditions for reaction at the boundary line. Before considering this question, the picture of these conditions probably requires amplification. At some place on the strip, at any moment, there must be a real boundary between wet and dry cellulose. Although the grosser, visible boundary can be made, by careful working, to remain stationary, the rate of evaporation is not under such minute control as to make the real boundary constant in position. It will therefore be subject to a series of irregularly advancing and receding tides, giving a "beach" area in which, during part of the time, the fibres will be drying after immersion. They will not be covered by a comparatively thick film of water as in the wet part, but they will contain more water, and be more fully swollen, than in the dry part. The access to oxygen molecules, which do not have to diffuse through a thick water film, should therefore be greater than in the fully wetted part. The fibres, being more fully swollen, should be more reactive than in the dry part. These two factors, acting together, may be sufficient to account for a specially high rate of reaction between cellulose and oxygen in the beach area. An objection to this simple picture, which depends for its feasibility on the presence of sharp oxygen concentration gradients in passing over the region between truly wet and truly dry cloth, is the absence of any indication of pronounced change in the rate of brown line formation when the oxygen content of the external atmosphere is greatly increased or greatly diminished. This objection could be circumvented in part by assuming the presence on the surface of the cellulose of an occluded oxygen layer, which might be dissolved, and thereby diluted, by the presence of free water.

The concept of a region intermediate between fully wet and fully dry may be applied in a different way. If it is small in depth at any one time, the hairs across which it occurs are being subjected to a series of irregular and highly localised swellings and dryings, and this may generate sufficient mechanical strain to initiate a disruption of the cellulose structure, followed by an increased chemical attack on the disintegrated material.

Owing to the small weight of substance which seems to be necessary to produce a visible brown line, this suggestion may be more probable than would at first be imagined.

An interesting field for speculation is the form and characteristics of the electrical charge distribution in the region between wet and dry. Cellulose in contact with water acquires a negative charge, which has been explained as a segregation of ions into an electrical double layer with the positive ions on the outside. As the film of water over the fibres which are situated at the extreme edge of the wet area thins out during one of the periods of drying (i.e. during a "receding tide"), it is possible that a disturbance of the double layer may take place in such a way that local high concentrations of hydrogen ions are set up, and that these may accelerate hydrolysis of the cellulose in the same locality. With the constant repetition of the process a significant amount of hydrolysed cellulose might accumulate.

Further attempts to provide explanations of the effect are likely, at the present stage, to be as speculative as those which have been made above. It is considered that little decisive progress can be made until the task of freeing the whole system much more completely from oxygen has been undertaken, and until the criteria of purity in cellulose have been re-examined.

Before closing the discussion, attention may again be directed to the significance of the distinctive properties of the two different types of modified cellulose which have been shown to be produced in the evaporation process. The one is coloured, soluble in water, fluorescent, and reducing; the other is insoluble, colourless, not specially fluorescent, and has some reducing properties and an enhanced Methylene Blue absorption. Fluidity values for the portions of the cloth in which this second form is detected are only slightly different from those of the adjacent areas. It would be interesting to know whether these two kinds of product represent—

(*a*) Transformation products each deriving from different kinds of chemical structure to be found initially in the natural cellulose;

(*b*) Different stages in the modification of the same cellulose molecules; or

(*c*) The results of a process in which cellulose molecules are attacked in such a way that small fragments are broken off to provide the soluble brown product, leaving residues of considerable molecular length, but with new end-groups, and probably retaining their original positions in the fibre structure.

In order to decide these questions, it is almost certain that evaporation experiments will have to be carried out on such a scale as to furnish much larger weights of the products.

We should like to express our sincere thanks to Mr. F. Scholefield for suggesting this problem for investigation, and for frequent advice and encouragement during the course of the work.

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ERRATUM

Report of the Committee on the Dyeing Properties of Wool Dyes (J.S.D.C., **66**, 221 (April 1950))— In the first column "Alizarine Light Blue 4GL (YDC)" should be deleted.

Notes

Proceedings of the Council

At a meeting of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 19th April 1950, the proceedings included the following items of interest—

ELECTION OF CHAIRMAN— Mr. Fred Scholefield (President of the Society) was elected Chairman of the Council for 1950–51.

ELECTION OF VICE-CHAIRMAN— Mr. F. L. Goodall was elected Vice-chairman of the Council for 1950–51.

NEW *EX-OFFICIO* MEMBERS OF COUNCIL— It was reported that the following had recently become *ex-officio* members of the Council—

Mr. R. L. Robinson (*Chairman, Huddersfield Section*)

Mr. E. A. Swift (*Chairman, West Riding Section*)

Mr. C. C. Wilcock (*Chairman, London Section*).

SECOND CANADIAN TEXTILE SEMINAR— It was reported that Mr. C. C. Wilcock and Mr. R. A. McFarlane had agreed to contribute a paper on *Trends in Dyeing and Finishing Machinery*. The

President stated that he had received a very cordial letter from the Chairman of the Seminar expressing appreciation of the interest shown by the Society in the Seminar, which is being organised by the Textile Technical Federation of Canada (see J.S.D.C., **66**, 289 (May 1950)).

ANNUAL REVIEWS COMMITTEE— The resignation of Mr. F. M. Stevenson, owing to pressure of work, from the joint Annual Reviews of Textile Progress Committee was accepted with regret.

MEMBERSHIP OF COMMITTEES— The membership of the non-technical committees of the Society was reviewed for the forthcoming session.

REPRESENTATION ON EXTERNAL BODIES— The representation of the Society on external bodies was reviewed for the forthcoming session.

"COLOUR INDEX" EDITORIAL PANEL— It was agreed that Dr. H. H. Hodgson be invited to serve on the Panel.

MEMBERSHIP— Twenty-six applications for ordinary, two for junior, and two for life membership were approved.

Meetings of Council and Committees
May

Council— 10th
Finance— 10th
Publications— 16th
Colour Index Editorial Panel— 1st and 22nd
Fastness Tests Co-ordinating— 25th
Terms and Definitions— 24th

Board of Trade
Technical Information and Documents Unit

The T.I.D.U. has moved from 40 Cadogan Square, London S.W.1, to Lacon House, Theobalds Road, London W.C.1 (*Telephone* CHAncery 4411). Reports, documents, and other records of German wartime industrial developments will continue to be at the disposal of interested British firms. T.I.D.U. will also continue to disseminate to British industry research reports which have been made available by the U.S. Government for this purpose, to arrange for the publication of selected Government Research Reports, and to act as National Centre for the United Kingdom in the O.E.E.C. Documents Exchange Scheme.

Among other departments of the Board of Trade which are moving into Lacon House are the Paper Control (Newsprint), Home Flax Directorate, Leather Control, Timber Control, and the Exhibitions Branch.

International Organisation for Standardisation

M. Caquot (France), a distinguished civil engineer, has been elected President of the International Organisation for Standardisation (I.S.O.) in succession to Mr. Howard Coonley (U.S.A.). Membership of the I.S.O. is confined to representatives of the national standards bodies throughout the world. The British Standards Institution represents the United Kingdom, and implements international recommendations by reference to them in the appropriate British Standards.

New Books and Publications

Synthetische Methoden der Organischen Chemie

By W. Theilheimer. Pp. viii + 412. Basle and New York: S. Karger. 1949. Price, 40 Swiss francs.

This compendium of synthetic processes employed in organic chemistry is a continuation of the general scheme adopted in the previous volumes of 1945 and 1948 for the classification, with brief description and reference, of new preparations of organic compounds together with any improvements of earlier methods (cf. J.S.D.C., **64**, 399 (Dec. 1948)). The publications dealt with are mainly from the years 1946–7 with some, where possible, from 1948, and American work has received special attention as a compensation for its paucity in the second volume. The comprehensive index includes the indexes of the two previous volumes, and, since it has not yet been found possible to publish an English translation, an index key in English has been added. The printing is good and the brevity of description is admirable, thereby enabling the inclusion of no fewer than 771 preparations in 359 pages, while the accompanying formulæ greatly assist the interpretation of the concise text. The book is an indispensable tool for the research organic chemist.   H. H. HODGSON

A.S.T.M. Standards on Soaps and other Detergents

Prepared by A.S.T.M. Committee D–12 on Soaps and other Detergents. Pp. ix + 124. Philadelphia: American Society for Testing Materials. 1949. Price, $1.75.

This book includes Standard Specifications for Soaps and Alkalis, Methods of Analysis, Sampling, etc., together with Standard Definitions of Terms employed.

Specifications for various soaps and alkaline detergents are given in full, and in general may be considered reasonable and not such as to cause technical difficulty in manufacture of the various products, but at the same time the resultant soaps would be of good quality and capable of easy manufacture within the limits set forth.

The section devoted to Chemical Analysis of Soaps and Soap Products represents modern analytical practice in the analysis of soaps, and the methods employed are accurate and up to date. It is to be noted that the determination of unsaponified matter is carried out by difference after determining unsaponified plus unsaponifiable matter together; this may not always be very satisfactory, and carrying out the two tests separately would be

advisable for check purposes. Mixed alkalis are determined by the chloroplatinate method and not by the perchlorate method.

Analysis of soaps containing synthetic detergents is also covered, but it is to be regretted that no method is suggested for the identification of the various types of soapless ingredients; this is badly needed, but not, so far as we are aware, at present available.

Analysis of Industrial Metal Cleaning Preparations follows standard methods, and there is also included Total Immersion Corrosion Tests of Water Soluble Aluminium Cleaners of the non-etching type, both qualititative and visual.

On the whole, the book is a satisfactory production, drawn up with care and likely to cover all normal requirements in connection with the various products mentioned therein.   F. G. REYNOLDS

Reports on German Industry

Röhm & Haas, Darmstadt
Acrylic Resins in Textile Finishing and Sizing
Paraffin Wax Emulsions
FDX 759*(PB 82,178; Microfilm I 294).

Microfilm of 253 reports written in German during 1932–46. There are a large number on the production of various acrylic resins and their use in textile finishing and sizing. A considerable number of reports deal with the production of tanning agents, e.g. by treating acrolein diacetate with ammonia, while others deal with the production of paraffin wax emulsions for various purposes.   C. O. C.

Röhm & Haas, Darmstadt
Acrylic Resins as Textile Finishes, Sizes, etc.
Acrylic Fibres— Analytical Methods
FDX 761* (PB 74,520; Microfilm I 296).

A microfilm of 132 items, some of which consist of more than one document, written in German during 1939–44. The first part of the film contains a series of reports dealing with investigations into the production of acrylic resins and their use in the crease-resisting of textiles, as adhesives, etc. Then follows a series of reports on the spinning of Plexigum and the properties of the resulting fibres. A further series of reports deals with the production, testing, and application of resin sizes. The last part of the film contains 20 analytical methods used in the Röhm & Haas laboratories.   C. O. C.

Kalle & Co. Chemische Fabrik, Wiesbaden-Biebrich
Cellulose Derivatives, Polyamides, Dyes and
Photographic Chemicals, Gums and Adhesives,
Desizing Agents
FDX 728* (PB 74,292; Microfilm IFF).

A collection of monthly laboratory reports, written in German during 1931–44. Many aspects of the manufacture and use of cellulose derivatives, pancreatic enzymes, polyamides, proteinases, adhesives, diazo compounds and coupling components, sensitising dyes, etc. are discussed.   C. O. C.

Carbo Norit Union, Bad Homburg
Manufacture of Activated Carbon and its
Application from 1935 to 1945
FDX 745* (PB 74,540; Microfilm I 310).

A microfilm of 135 reports, technical correspondence, etc. in German. A large number of them deal with the impregnation of staple rayon fabrics with activated carbon both for surgical purposes and as gas-protective clothing. There are two reports dealing with the successful use of activated carbon in the dyeing of acetate rayon and mixtures of 50% wool, 12% acetate rayon, and 38% cellulose fibres.   C. O. C.

I.G. Farbenindustrie A-G., Ludwigshafen
Organic Compounds— Prevention of the
Clotting of Fast Scarlet G Base
FD 2224/49* (part of PB 17,658).

Microfilm of 21 papers presented to an I.G. inter-works conference in 1935. One of them states that treating Fast Scarlet G Base (9 parts 4-nitro- and 1 part 6-nitro-o-toluidine) with a 2–5% aqueous solution of Emulphor O, or better still very dil. H_2SO_4, prevents this product from becoming lumpy on storing.   C. O. C.

I.G. Farbenindustrie A-G., Leverkusen
Dyes, Intermediates, and other Organic
Compounds
FDX 738* (PB 73,913; Microfilm N 78).

Microfilm of 215 laboratory reports, written in German during 1929–44, on various aspects of dye and intermediate production, with a few reports on miscellaneous matters such as starch thickeners for printing pastes, rubber chemicals, etc. Many of the reports deal with azoic and carbazole dyes. Several reports deal with the Ergansoga range, and it is stated that Ergansoga Koening RNS was the same product as Azol Printing Orange R. Another report deals with the use of Nigrosines as food dyes.   C. O. C.

I.G. Farbenindustrie A.-G., Wolfen
Intermediates— Acetate Rayon, Fur, and
Leather Dyes
FD 2234/49* (part of Microfilm PB 17,658).

Microfilm copy of 12 papers read at an I.G. inter-works conference in 1935. Eight of them deal with intermediates, including 2-hydroxymethyldihydrobenzoxazine, which was being studied as a coupling component. Another paper deals with quinolines from the aminonaphthols, especially as intermediates for acetate rayon dyes. Yet another paper deals with a brown leather dye from 1:1'-dinaphtho-2:2'-carbazole. Mono- and di-hydroxynaphthalenes are discussed for use as Ursatins, the constitution, hue, and fastness properties of nine of them being given; there is also a very brief account of other mono- and polyhydroxy compounds intended for the same range, details regarding 28 of them being tabulated.   C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Ferrigans— Dyes— Detergents and Textile
Auxiliaries
FD 1192/49* (PB 74,808).

A microfilm of a variety of papers and reports, in German, dated 1926–44, but most of them being written between 1940 and 1944, dealing with research and development in various fields of organic chemistry. Among them are the following (authors' names are given in parentheses)—

Ferrigan P, a New Iron Tanning Agent (Krzikalla) and *New Iron Tanning Agents— Ferrigans* (Krzikalla and Otto)
Hydroxyethylated Azo Dyes of the Diphenylamine Series (Krzikalla and Garbsch)
Azabenzanthrone (Köberle and Rohland)
Phenyl-azolo-anthraquinone Dyes (Schlichting)
Mode of Action of Levelling Agents (Valko)
Molecular Mechanism of Pigment Washes (Valko)
Constitution of the Water-soluble Calcium Compounds of Trilon A and Ma 416 (Pfitzner and Valko)
Studies of the Naphthindenone Series—5-Azabenzanthrone
Organic Water-softening Agents
p-Aminophenones and Wool Dyes from them
Particle Size in Solutions of Leuco Vat Dyes
Fast Development Dyes on Wollstra with Neutral Water-soluble Substantive Naphtols— IV
Azo Dyes containing Aliphatic Radicals (Krzikalla)
Fast Development Dyeing by Self-coupling with Substantive Aminonaphthols—II

New Aftertreatment for improving the Fastness of Diazo-tisable Azo Dyes (Krzikalla)

Dimethyl Palm-kernel Fatty Amine as Precipitant for Zapon Fast Dyes (Krzikalla)

Fast Development Dyeing by Self-coupling with Amino-naphthol Azo Dyes (Krzikalla)

Dyes from m-Aminophenylmethylcarbinol (Krzikalla)

A New Group of Water-soluble Dyes (Krzikalla)

Technically Applicable Testing of Detergents and Textile Auxiliaries from the Olefins of Ruhrchemie A.-G. (Amende)

Highly Basic Polyamides (Krzikalla and Hochadel)

Blue Pigment from 2-Chloro-5-aminobenzoic Acid

Blue Vat Dye from 1-Aminoanthraquinone-2-aldehyde and Barbituric Acid

Red Acid Dyes of the Anthrapyrimidine Series (Schlichting)

Yellow Pigments from ω-Aminoacetophenol-o-carboxy-amide (Schlichting and Klager)

Explanation of the Constitution of Ciba Scarlet BB for Nitro Lacquers   C. O. C.

Vereinigte Glanzstoff-Fabriken, Obernburg
Viscose Rayon and Polyamide Fibre Research
FDX 754* (PB 82,173; Microfilm 299 D).

Ninety research reports written in 1942–45, all in German except for two, which are in French. They deal mainly with various aspects of the production of viscose rayon, including dope dyeing and the effect of variations in the manufacturing process on dyeing properties. There are also a few reports on manufacture and melt-spinning of polyamides and one on the production of glass fibres.   C. O. C.

Zellwolle- und Kunstseide-Ring G.m.b.H., Berlin
Papers circulated to Members from April to November 1944
FDX 756* (PB 82,155; Microfilm B 256).

Some 60 reports, in German, dealing mainly with various aspects of the manufacture of cellulosic rayons and to a lesser extent with polyvinyl fibres, together with some miscellaneous subjects.   C. O. C.

Dynamit A.-G., Troisdorf
Polyamides—Heating of Calenders and Rolls Drying by Ultra-short waves
FDX 730* (PB 74,768; Microfilm M 157).

Among a large number of reports, in German, dealing with explosives there are one (frames 1628–30), written in 1946, describing the melt-spinning of polyamides at the Aceta works, a second (frames 1631–35), dated 1941, giving information on the heating of calenders and rolls, and a third (frames 1653–57), written in 1941, surveying the ultra-short wave method of drying fibres.   C. O. C.

Institut für Chemische Technologie Synthetischer Fasern, Breslau
Swelling of Staple Fibre
K. Lauer. FD 1941/49* (PB 18,432).

Microfilm copy of three papers written in German in 1944. The first is entitled *Effect of Catalysts on the Swelling Value of Staple Fibres*, and the second and third are both entitled *Effect of Catalysts on the Formaldehyde Treatment of Viscose Rayon.*   C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Does Dyeing cause Disruption of the Cellulose Molecule?
FDX 770* (PB 82,005; Microfilm X 40).

Among many miscellaneous reports there is one of 19 pp. (Frames 2758–2766), written in German in 1942, describing 18 tests each with Vistra, Duraflex, Cuprama, and cotton to see whether dyeing lowers the degree of polymerisation of cellulose.   C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen
Salicylic Acid Resins for Paper Sizing
FD 2760/49* (PB 33,057 (part of PB 17,670)).

Microfilm copy of a report, written in German in 1941, dealing with tests made with salicylic acid resins and their comparison with Luresin F for mixing with rosin to produce sizes for paper. A naphthalene–*iso*propylnaphthalene–salicylic acid–formaldehyde resin was found to be superior to Luresin F in every respect except light fastness.   C. O. C.

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

Abstracts from British and Foreign Journals and Patents
(*The Titles of Patents are abridged and modified*)

I—PLANT; MACHINERY; BUILDINGS
PATENTS

Saponifying Organic Ester of Cellulose Yarns in Cake Form. G. W. Seymour, W. J. Elvin, D. Y. Miller, and Celanese Corpn. of America.
                 U.S.P. 2,487,833.

Saponifying Cellulose Ester Rayon in Package Form. W. Whitehead, J. B. Steiding, and Celanese Corpn. of America.   *U.S.P.* 2,487,841.

Cone for Dyeing Yarn. R. A. Russell and Russell Manufacturing Co.   *U.S.P.* 2,489,465.

Package Drying. J. G. Wiegerink and American Viscose Corpn.   *U.S.P.* 2,490,938.

Drying of wound packages of yarn or fabric can be economically done, with improved fibre qualities in the final dried product, by first heating by high-frequency induction until 33–80% of the moisture originally present has been removed, and then completing drying by circulating hot air through the package.   C. O. C.

Apparatus for making Cemented Pile Fabric. E. B. Allen.   *B.P.* 634,131.

Coating Webs of Paper or the like. Vickers-Armstrong Ltd. and J. I. Nasmith.   *B.P.* 634,220.

The web is fed under tension over an idler stripping roller, with which it makes sufficient contact to rotate the roller in unison with the varying speed of the web. The coating material is fed to the stripping roller by the surface tension of the former from a feed roller partly immersed in a reservoir containing the coating material but not in contact with the stripping roller. A constant thin and even coating is obtained.   C. O. C.

Coating Sheet Material. A. H. Williams and E. F. Taylor.   *B.P.* 634,950.

Blankets for Offset Printing. L. R. Liles, E. W. Chapman, and B. F. Goodrich Co. *U.S.P.* 2,489,791.

Hosiery Drier. S. Pikor.   *U.S.P.* 2,490,322.

A hanger has several bearing members having grooves and pivoted holding members, which can be placed in the grooves so as to cause hosiery placed upon the bearing members to adhere in the grooves. The holding members can then be raised to allow other articles to be placed upon the bearing members without the articles first placed there slipping out of position.   C. O. C.

Automatic Humidity Control. J. Stone & Co. Ltd., F. H. E. Read, and W. M. Smith.   *B.P.* 634,204.

Thermostats exposed to wet-bulb and dry-bulb temperatures are provided with auxiliary heating means by which they are caused to cycle. They are arranged to operate in unison at a particular R.H. and to actuate humidity-correcting means when they operate out of unison.
                 C. O. C.

Heating Chest for a Laundry Ironing and Pressing Machine. N.V. Machinefabriek Reineveld.
                 B.P. 634,242.

Steam Vacuum Finishers. Bill Glover Inc.
B.P. 634,698.

A steam vacuum finisher comprises a pedestal supporting a shallow pan; a perforated sheet, on which the garments are placed, covers the pan, inside which is a heating coil adjacent to the sheet, means for injecting steam, and an air ejector to apply vacuum. A pedal-operated mechanism manipulates the valve system as desired.   J. W. B.

Garment-spotting Machine. Bill Glover Inc.
B.P. 634,898.

An auxiliary spotting head is provided to deal with sleeves, pockets, trouser legs, etc.   C. O. C.

Pasting Skins— Stretching and Drying Tanned Skins upon Boards or Plates. R. L. Griffin, N. Y. Moore, and A. C. Lawrence Leather Co.
U.S.P. 2,488,907.

Conditioning or Lubricating Carded Fibres. Monsanto Chemical Co. (VI, p. 339.)

Electronograph Printing. W. C. Huebner. (IX, p. 341.)

II— WATER AND EFFLUENTS

PATENT

Automatic Addition of Softening or other Reagents to Water. R. H. Froude.   *B.P.* 634,557.

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Composition and Structure of Technical Emulsions.
J. H. Goodey. *Roy. Australian Chem. Inst. J. & Proc.*, **16**, 47–75 (1949): *Chem. Abs.*, **44**, 902 (10th Feb. 1950).

A general theory of emulsions, applicable to technical problems, is attempted on the basis of existing empirical data. The technical oil–water emulsion is regarded as a system of four components— the dispersion medium, the disperse phase, the coupling agent (I) (an oil-soluble substance containing a polar group), and the emulsifying agent (II) (a water-soluble substance with a hydrocarbon radical attached to an ionisable group). The factors controlling adsorption of I and II at the oil–water interface are deduced from study of their respective interfacial tension–concentration curves. Where an aqueous solution of II is in contact with an oil phase to which increasing amounts of I are added, the interfacial tension passes through a minimum, indicating maximum adsorption, when I and II are present in a certain proportion. When excess I is present, however, adsorption at the interface is considerably reduced, and II tends to pass into the oil phase. The processes of adsorption and desorption at the surface of the emulsoid oil droplet, considered as an isolated unit, are then discussed, and a model droplet is proposed.   C. O. C.

Preparation of Cholesterol from Wool Grease by means of Addition Products. J. T. Hackmann. *Rec. Trav. chim.*, **69**, 433–438 (March 1950).

Fractionation of Starch. R. S. Higginbotham. *J. Textile Inst.*, **40**, T 783–T 808 (Dec. 1949).

III— The Amylose-Iodine Reaction

By using a much wider range of iodine concentrations than previously employed it has been shown that the absorption of iodine by amylose does not reach a limiting value, other than that imposed by the limited solubility of the iodine. It has been confirmed that the absorption takes place in two stages. In the first, there is no simple relation between the amount of iodine absorbed and the free iodine concentration, and the absorption spectrum of the absorbed iodine remains constant. In the second stage, the amount of iodine absorbed is a linear function of the logarithm of the free iodine concentration, and the absorption spectrum changes in a manner suggesting that the additional iodine is being forced into amylose helices which already contain iodine.

IV— The Amylopectin-Iodine Reaction

The composition and absorption spectra of amylopectin-iodine complexes and glycogen–iodine complexes have been determined over a wide range of iodine concentrations. If the concentration of the free iodine is sufficiently high, the amylopectins absorb as much iodine as the amyloses. The inference that amylopectins absorb iodine partly by a helix mechanism involving chains of iodine molecules and tri-iodide ions, and partly by adsorption of single iodine molecules or single tri-iodide ions, is supported by spectrophotometric data. The proportion of iodine bound by the helix mechanism varies with the total amount of iodine absorbed and with the identity of the amylopectin. These variations may be related to the distributions of branch lengths in the amylopectins.
W. K. R.

Chromatography of Soluble Starches. M. Ulmann. *Kolloid-Z.*, **116**, 10–18 (Jan. 1950).

Selective adsorption of starches is carried out with a column of Al_2O_3. Differently coloured adsorption bands, dark blue, light blue, and light violet, are then obtained with I_2–KI. Better separation of the individual zones is brought about by pretreatment of the Al_2O_3 with dil. HCl.   B. K.

Acid Colloids of Resins. American Association of Textile Chemists and Colorists, Rhode Island Section. *Amer. Dyestuff Rep.*, **38**, P 842–P 852 (28th Nov. 1949).

The reaction products of seven melamine–formaldehyde resins and four urea–formaldehyde resins with fifteen inorganic and organic acids have been studied as acid colloids of resins, which require only a low curing temperature. When applied to cotton, such resins cause no loss in tensile strength and confer superior abrasion resistance and retention of handle after laundering. Acid colloids provide a suitable medium for the application of pigment dyes, and are also useful in improving the wash and light fastness of direct dyeings on cotton and viscose. A. S. F.

PATENTS

Dispersing Agent. T. L. Wilson, J. A. Davison, and United States Rubber Co.   *U.S.P.* 2,489,943.

The product obtained by heating the half ester of 2-ethylhexane-1:3-diol and maleic acid, and then treating the resulting maleic alkyd resin with an alkali bisulphite to produce a water-soluble polymeric ester of 2-ethylhexane-1:3-diol and sulphosuccinic acid, is a non-foaming dispersing agent which does not impart discoloration on ageing to white, colourless, or light-coloured synthetic resins.   C. O. C.

Aqueous Solutions of Water-insoluble Substances. Taubmans Ltd.   *B.P.* 634,499.

Clear aqueous solutions of water-insoluble compounds which are soluble in sulphated esters, e.g. of dibutyl phthalate soluble in sulphated butyl oleate, are prepared by mixing the compound in liquid form with sulphated butyl oleate or the Na, K, or NH_4 salt thereof, and adding the resulting fluid mixture to water.   J. W. B.

Detergent from Seaweed. J. de la Vega Samper.
B.P. 634,179.

Seaweed mucilage is treated with caustic lye until saponified. The product is used as a substitute for soap. C. O. C.

Polyalcohol–Fatty Acid–Aliphatic Amine Combinations useful as Textile Assistants. A. A. Cook, I. Sapers, and Arkansas Co. Inc. *U.S.P.* 2,491,478.

A high yield of unusually effective detergent, wetting, and emulsifying agents is cheaply obtained by treating a high-mol.wt. fatty acid, e.g. a C_{8-24} acid, at a relatively low temperature, e.g. < 135°C., first with a polyethylene glycol and then with an aliphatic amine.   C. O. C.

Insect-proofing Agents. J. R. Geigy A.-G.
B.P. 634,915.

Compounds of formula $R^1\cdot CH(OH)\cdot C(NO_2)R^2R^3$ (R^1, R^2, and R^3 = H or univalent organic radicals), especially $Cl_3C\cdot CH(OH)\cdot CH_2NO_2$, are insect-proofing agents for textiles, etc.   C. O. C.

Polyvinylpyridinium Halides — Surface - active Agents, Fungicides, Insecticides, and Bactericides. L. M. Richards and Du Pont.
U.S.P. 2,487,829.

Water-soluble poly-N-alkyl-vinylpyridinium halides are obtained by treating an alkyl halide with a polyvinylpyridine dissolved in an inert solvent.   C. O. C.

Antimonyl Derivatives of Polyhydric Phenols as Antioxidants. B. A. Hunter and United States Rubber Co. *U.S.P.* 2,488,975.

0·1–5·0% of an antimonyl polyhydric phenol containing an *o*-dihydroxy grouping, e.g. antimonylcatechol, acts as an antioxidant when added to oil, rubber, etc. C. O. C.

Reducing Foaming of Liquids. Ciba Ltd. *B.P.* 634,197.

A mixture of a water-soluble organic solvent other than an alkyl ether of ethylene glycol, e.g. *iso*propyl alcohol, and an alcohol or phenol having at least one open chain of > 4 C and sparingly soluble in water, e.g. 2-ethylhexanol or *p-tert.*-amylphenol, when added to aqueous liquids reduces their tendency to foam. C. O. C.

Resin Emulsion Base Wrinkle Composition. N. T. Beynon. *B.P.* 634,986.

A wrinkle-drying coating composition for application to cloth, paper, etc. contains an uncooked wrinkling or conjugated double-bonded oil and an aqueous dispersion of an acrylic ester, polyvinyl acetate, or melamine– or urea–formaldehyde resin. C. O. C.

Wrinkle-drying Compositions containing Dextran Derivatives. E. L. Luáces and New Wrinkle Inc. *U.S.P.* 2,490,070.

Addition of dextran derivatives, e.g. dextran benzyl ether or dextran acetate, to wrinkle-drying coating compositions enables wrinkle patterns and textures hitherto unobtainable to be produced, the pattern or texture being controlled by the particular dextran derivative used and/or the amount of it and/or by varying the temperature during the initial drying or texturing period. C. O. C.

Adhesives for Nylon. I.C.I. Ltd. *B.P.* 634,422.

Strong nylon–nylon adhesion is provided by an adhesive consisting of a solution of nylon in a solvent mixture of phenol, cresols, xylenols, and polyphenols, in carbolic oil, or in cresol only. J. W. B.

Derivatives of *s*-Dimethyl-*p*-phenylenediamine— Textile Auxiliaries, Intermediates, and Disazo Dyes. C. F. H. Allen, J. V. Crawford, G. F. Frame, J. E. Jones, E. R. Webster, and C. V. Wilson. (IV, p. 333.)

Stabilised Dry Saponified Rosin Sizes. A. C. Dreshfield and Hercules Powder Co. (XI, p. 342.)

Plastic Fungicidal Composition. H. E. Smith and Insl-X Corpn. (XIII, p. 343.)

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Substitutions in Aromatic Nuclei. A. E. Korvezee and F. E. C. Scheffer. *Rec. Trav. chim.*, **69**, 496–503 (March 1950).

In the bromination of naphthalene in the gaseous phase, and in the absence of a catalyst, two pairs of parallel reactions occur, of the first order with respect to the bromine as well as to the naphthalene concentration. One pair predominates at low and the other at higher temperatures. H. H. H.

Dissociation and Tautomerism of some Quinone Monoximes. E. Havinga and A. Schors. *Rec. Trav. chim.*, **69**, 457–467 (March 1950).

A study of ultra-violet absorption spectra at various pH values of the solutions in water of quinone monoxime, 1:4-naphthaquinone oxime, 9:10-anthraquinone oxime, and the higher-melting form of 3-chlorobenzoquinone-4-oxime indicates the existence of a simple dissociation equilibrium. The pK's of dissociation were determined to be 6·21, 8·01, 9·78, and 5·68 respectively. The tautomerism between quinone oxime and nitrosophenol forms in the solutions in water of compounds of this type is considered to be based upon this dissociation equilibrium with a mesomeric ion, formed from the two tautomers by release of a proton. The curves for the lower-melting 3-chloro-4-nitrosophenol appeared to indicate a more complicated system. H. H. H.

Action of Copper on some Aryldiazonium Sulphates and the Isolation of Copper Salts. H. H. Hodgson and J. Habeshaw. *J.C.S.*, 405–406 (Jan. 1950).

When copper reacts with aryldiazonium sulphates, deamination occurs to an extent which varies according to the amine employed, while the amount of phenol (or

naphthol) which is directly isolatable by steam-distillation is generally less than expected. In the non-volatile residues, however, are white or yellow copper compounds which, from their copper contents, appear to possess the structure Ar·O·Cu (cf. also Cowdrey and Davies, *J.C.S.*, S 48 (1949)). H. H. H.

1-(*x*-Hydroxyphenyl)naphthalene (Discrepancies in the Literature— VIII). J. Van Alphen and G. Drost. *Rec. Trav. chim.*, **69**, 284–286 (March 1950).

Phenol when heated either with naphthalene - 1 - diazonium chloride or its zinc chloride double salt gives *a-o*-hydroxyphenylnaphthalene, as claimed from the lack of identity of its methyl ether with that of *a-p*-methoxyphenylnaphthalene. H. H. H.

Isomerisation of Labile Diphenyl-4:4′-bisdiazocyanide in Solution. D. D. Brown, R. J. W. Le Fèvre, and R. N. Whittem. *J.C.S.*, 185–188 (Jan. 1950).

The spontaneous formation of the stable *trans-trans*-from the unstable *cis-cis*-diphenyl-4:4′-bisdiazocyanide is found to proceed by a complex mechanism: viz. in benzene solution by first-order kinetics with an activation energy of 26·9 kg. cal./g.-mol., but in the polar solvents *o*-dichlorobenzene, pyridine, and nitrobenzene by less simple kinetics. The suggestion is made that two consecutive first-order inversions occur, with the unknown *cis-trans*-variety as an intermediate. This requires the assumption that, in benzene solution, the rate of one of the inversions is not significant kinetically, and that the overall change in this solvent is governed by only one of the two rates. H. H. H.

***o*-Mercapto-azo-compounds. I— The Coupling of Tetrazotised 2:2′-Diaminodiphenyl Disulphide with *β*-Naphthol.** A. Burawoy and C. Turner. *J.C.S.*, 469–477 (Feb. 1950).

A general method for the preparation of the hitherto unknown *o*-mercaptoazo compounds is developed. Only monodiazotisation of 2:2′-diaminodiphenyl disulphide occurs in dilute acid, the product decomposing spontaneously to yield benz-1-thia-2:3-diazole, but the tetrazonium salt is formed and is stable in concentrated sulphuric acid, although it is decomposed by water to form the above diazole. Coupling occurs when the concentrated sulphuric acid solution is added directly to solutions or suspensions of *β*-naphthol in aqueous sodium hydroxide, sodium carbonate, sodium hydrogen carbonate, sodium acetate, or pyridine, but three different reactions are encountered which proceed from an initial intermediate compound (I), viz. decomposition of (I) in sodium


(I)
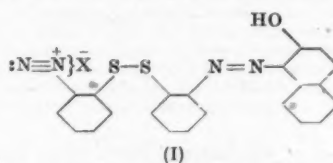
hydroxide and carbonate solution to benzthiadiazole and unstable *o*-(2-hydroxynaphthalene-1-azo)benzenesulphenic acid, which then undergoes spontaneous disproportionation in sodium hydroxide solution to di-*o*-(2-hydroxynaphthalene-1-azo)phenyl disulphide and *o*-(2-hydroxynaphthalene-1-azo)benzenesulphinic acid, whereas in sodium carbonate a condensation occurs with a second molecule of *β*-naphthol to form *o*-(2-hydroxynaphthalene-1-azo)phenyl 2-hydroxy-1-naphthyl sulphide. (I) is sufficiently stable in either sodium hydrogen carbonate or acetate or pyridine to allow coupling with a second molecule of *β*-naphthol in preference to degradation. H. H. H.

Synthesis of Dye Antipodes for Histological Stains— I. F. Kögl, J. G. Faber, and Z. C. De Boer. *Rec. Trav. chim.*, **69**, 482–491 (March 1950).

Enantiomorphous phenazine derivatives formed by condensation of D- and L-camphorquinones with 2:3:6:7-tetra-aminophenazine have been used for the staining of normal and diseased animal tissues. No visible differences between the intensities of the stains were observed. H. H. H.

Derivatives of s-Dimethyl-p-phenylenediamine— Textile Auxiliaries, Intermediates, and Disazo Dyes. C. F. H. Allen, J. V. Crawford, G. F. Frame, J. E. Jones, E. R. Webster, and C. V. Wilson. *J. Org. Chem.*, **13**, 666–670 (1948).

s-Dimethyl-p-phenylenediamine or its oxalate reacted readily with aliphatic acid chlorides, aromatic carboxylic or sulphonic acid chlorides, and 2:4-dinitrochlorobenzene to produce compounds—
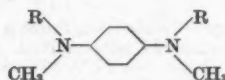
(R = stearoyl, palmitoyl, $CH_3 \cdot O \cdot CO \cdot [CH_2]_4 \cdot CO-$, chloroacetyl, p-nitrobenzoyl, o-sulpho-p-nitrobenzoyl, p-nitrophenoxyacetyl, 1-nitro-2-naphthoxyacetyl, m- and p-nitrobenzenesulphonyl, and 2:4-dinitrophenyl). When R = stearoyl or palmitoyl, the compounds are softening agents for textiles. When R = chloroacetyl, the compound reacted with pyridine to give the surface-active bisquaternary salt—
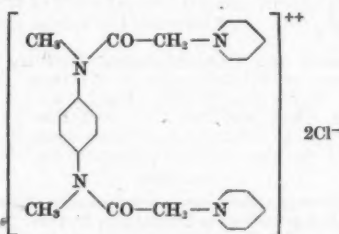
Diamines were produced from the compounds containing two nitro groups by reduction in presence of Raney nickel, and from the compounds containing four nitro groups by selective reduction with Na_2S. By tetrazotising these diamines and coupling with various coupling components, 25 disazo dyes for wool, cotton, and acetate rayon were prepared. Thus—
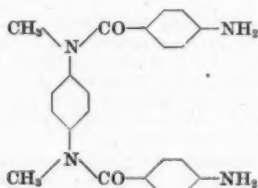
prepared by reduction of the p-nitrobenzoyl compound, was tetrazotised and coupled with 1-naphthol-5-sulphonic acid to give an orange wool dye, with 2-benzoylamino-5-naphthol-7-sulphonic acid to give an orange cotton dye, and with NN-di(β-hydroxyethyl)aniline to give a yellow acetate rayon dye.   E. S.

Preparation and Separation of 2-Amino-6-hydroxy-8- and -9-methylpteridines. Methylpteridine Red. P. Karrer and R. Schwyzer. *Helv. Chim. Acta*, **33**, 39–45 (Feb. 1950).

The condensation of 2 : 4 : 5 - triamino - 6 - hydroxy - pyrimidine with acetol in the presence of hydrazine gives a mixture of 2-amino-6-hydroxy-8- and -9-methylpteridines, which are separated by fractional crystallisation of their acetyl derivatives first from alcohol and then from water. This mixture also arises from the condensation of 2 : 4 : 5 - triamino - 6 - hydroxypyrimidine with dihydroxyacetone without any addition of hydrazine. Methylpteridine Red is formed when the above mixture is heated with 20% H_2SO_4.   H. H. H.

Sulphur Dyes and Sulphurised Vat Dyes. I— Constitution of Hydron Blue. II— Cibanone Yellow R. K. H. Shah, B. D. Tilak, and K. Venkataraman. *Proc. Indian Acad. Sci.*, **28 A**, 111–124 (1948); **30 A**, 1–11 (1949): *Chem. Abs.*, **44**, 1709 (25th Feb. 1950).

I— A new constitution is proposed for Hydron Blue, in which polymerisation of thionated carbazole–indophenol units through sulphoxide linkages is postulated. Other

analogous indophenols can be similarly constituted. The new constitution for sulphurised indophenol dyes readily accounts for formation of a diacetic acid derivative from pyrogen indigo on the basis of the reaction between chloroacetic acid and the phenolic groups in leucopyrogen indigo. That polymerisation of thionated carbazole–indophenol units does not proceed through C–C linkages has been proved by the identity of the reduction products from carbazole–indophenol and from Hydron Blue, obtained by treatment with Raney nickel.

II— Cibanone Yellow R, previously assumed to be homogeneous (J.S.D.C., **51**, 50 (1935)) has been shown by chromatographic analysis to be a mixture of several materials. Elementary analysis of the major tinctorial component, curved orange needles (I), m.p. 368–370°c. (from $C_2H_5Cl_4$), corresponds to $C_{45}H_{26}O_7S$; this indicates three methylanthraquinone residues to one S atom. Anthraflavone was among other products isolated. Degradation of I by Raney-nickel reduction yielded a product which appeared to be 2-methylanthraquinone. Similar conclusions arose from a Clar reduction. Oxidation of I gave 2-anthraquinonecarboxylic acid. It is considered that the 2-methylanthraquinone residues are linked together through the CH_2 groups by the S atom instead of through a methylene bridge as previously suggested and that the structure is $A \cdot CH_2 \cdot S(:O)(:CHA) \cdot CH_2A$ (A = 2-anthraquinonyl).   C. O. C.

Indenonecarboxylic Acids and *allo*-Dunnione. R. G. Cooke and T. C. Somers. *Nature*, **165**, 314 (25th Feb.), 839 (27th May, 1950).

2-Hydroxy-3-*tert.*-butyl-1:4-naphthaquinone rearranges with aqueous alkali to an isomeric carboxylic acid (cf. the isomerisation of dunnione—Price and Robinson, *J.C.S.*, 1522 (1939)). It is found that the reaction is general with hydroxynaphthaquinones having n-, sec.-, or *tert.*-alkyl groups, the rate being greatest with the tertiary compounds. The isomeric acids produced are now found to be indenonecarboxylic acids, since 2-hydroxy-3-*iso*-propyl-1:4-naphthaquinone is found to rearrange into 2-isopropylindenone-3-carboxylic acid.   H. H. H.

Mechanism of the Rubrene Reaction. C. Dufraisse, J. Lefrancq, and P. Barbieri. *Rec. Trav. chim.*, **69**, 380–390 (March 1950).

The preparation and halochromic properties of bis-(p-dimethylaminophenyl)phenylethynylcarbinol are examined, and its subsequent conversion to rubrene is discussed. The impossibility of passing by the usual mechanism from this carbinol, or from one of its coloured salts, to the corresponding rubrene has favoured a radical rather than an ionic mechanism for the process. H. H. H.

Azomethine Dyes from Pyrazolone. R. Gerbaux. *Bull. Soc. chim. Belg.*, **58**, 498–521 (Dec. 1949).

The preparations of a large number of azomethine derivatives of pyrazolone are described, together with their absorption spectra in acetone, alcohol, a mixture of equal parts of acetone and water, and for some of the compounds in chloroform, benzene, and light petroleum. The influence of substituents on the displacements of the absorption maxima is discussed.   H. H. H.

Polymethin Dyes with a Carboxyl Group substituted in the Chain. P. Bruylants and A. Van Dormael. *Rec. Trav. chim.*, **69**, 321–328 (March 1950).

The syntheses are described of asymmetric carbocyanines and *mero*carbocyanines, and also of a rhodacyanine, each having a carboxyl or carbalkoxyl group substituted at the β-position of the chain, from oxalylmethylene derivatives of benzthiazole. Optical data for the new dyes are included.   H. H. H.

β-Anilinovinyl Derivatives of Heterocyclic Bases. I— Substituted Anilino Derivatives. A. Van Dormael, J. Jacken, and J. Nys. *Bull. Soc. chim. Belg.*, **58**, 477–486 (Oct.–Dec. 1949).

II—New Methods for the Preparation of a Double Hemicyanine. A. Van Dormael and A. De Cat, *ibid.*, **58**, 487–490 (Oct.–Dec. 1949).

Ultra-violet and Infra-red Absorption Spectra of *meso*-Carbethoxythiacyanine Base. J. Nys and A. Van Dormael. *Bull. Soc. chim. Belg.*, **58**, 491–499 (Oct.–Dec. 1949).

The infra-red spectrum of the *meso*-carbethoxythiacyanine base (I) indicates a strong conjugation of the

carbonyl group, which denotes a substantial contribution of the form (II) to the resonance hybrid. The steric implications are discussed, and the identity of the absorption maxima in the ultra-violet of the cyanine bases (I) and (III) considered to be fortuitous.

(I)   (II)

(III)

H. H. H.
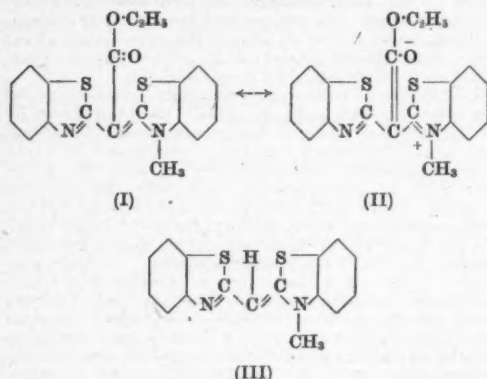
Colouring Matters of the Aphididæ. II— Colouring Matters from *Aphis fabæ*. J. P. E. Human, A. W. Johnson, S. F. MacDonald, and A. R. Todd. *J.C.S.*, 477–485 (Feb. 1950).

The isolation of four related colouring matters of a new type from the common bean aphid (*Aphis fabæ*) is described, viz. yellow *protoaphin*-fb, fluorescent yellow *xanthoaphin*-fb, fluorescent orange *chrysoaphin*-fb, and fluorescent carmine-red *erythroaphin*-fb. The last-named appears to be a polycyclic quinone containing two phenolic hydroxyl groups, and on oxidation with nitric acid it gives mellitic acid.   H. H. H.

Colouring Matters of the Aphididæ. III—Colouring Matters from *Tuberolachnus salignus*. H. Duewell, A. W. Johnson, S. F. MacDonald, and A. R. Todd. *J.C.S.*, 485–490 (Feb. 1950).

The four aphin colouring matters *protoaphin*-sl, *xanthoaphin*-sl, *chrysoaphin*-sl, and *erythroaphin*-sl have been isolated from the willow-tree aphid, *Tuberolachnus salignus*, and appear to be different from the aphins-*fb*. A method for the purification of the erythroaphins by partition between chloroform and sulphuric acid of varying strengths is described; mellitic acid is among their nitric-acid oxidation products.   H. H. H.

Bismuth as Hair Dye. H. Schwarz. *Seifen–Öle–Fette–Wachse*, **75**, 503 (1949): *Chem. Abs.*, **44**, 1231 (10th Feb. 1950).

Bi_2S_3 is formed on the hair from ammonium bismuth citrate solution and the S in the hair; 0·5% colloidal S is added to the solution as an accelerator. C. O. C.

Lubricating Oil Additives.   V — Dyes. V. A. Kalichevsky. *Petroleum Refiner*, **28**, (10), 125, 126 (1949): *Chem. Abs.*, **44**, 1687 (25th Feb. 1950).

Addition of some dyes may have an unfavourable effect on oil quality. Use of dyes is decreasing as the public becomes more aware that the colour of an oil has no relation to its performance. There are 31 patent references.
          C. O. C.

Physics and Chemistry of Pigments. C. E. Barnett. *Ind. Eng. Chem.*, **41**, 272–279 (Feb. 1949).

This paper reviews the literature on the application of formal chemistry and physics to the development of pigments, giving 121 references. The main aspects covered are refractive index, particle size, hiding power, and surface effects. The main problems to be solved by future research are stated.   A. S. F.

Titanium Dioxide Pigments. A. E. Jacobsen. *Ind. Eng. Chem.*, **41**, 523–526 (March 1949).

Evidence is presented that the chalking and fading behaviour of titanium dioxide paints is due to photochemical reactivity involving the vehicle. Direct correlation has been found between this behaviour and reactivity of both anatase- and rutile-type pigments in an alkyd paint. A photochemically reduced rutile titanium dioxide has been identified as α-Ti_2O_3. The photoreduction of

mandelic acid has been used to study the photochemical reactivity of titanium dioxide.   G. L.

Cadmium Sulphide. C. Severgini-Schinetti. *Pitture e Vernici*, **5**, 23–27 (1949): *Chem. Abs.*, **44**, 1720 (25th Feb. 1950).

Description of a plant for the manufacture of CdS by the reaction—

$$CdCO_3 + Na_2S \rightarrow Na_2CO_3 + CdS$$

The product is easily filtered, and its colour is stable.
          C. O. C.

Uranium Orange— Derivation from a Pentauranate with Formation of Uranium Red. A. Chrétien and G. Tridot. *Compt. rend.*, **229**, 367–369 (1949): *Chem. Abs.*, **44**, 967 (10th Feb. 1950).

The electrical conductivity and the pH are measured as 0·1 N. uranyl nitrate is added to 0·1 N-Na_2S. The yellow precipitate first formed gradually changes to orange and back again to yellow, finally forming a yellow solution. The pH curve shows three inflection points, at which there are also breaks in the resistance curve. These breaks correspond to yellow $5UO_3,Na_2O$, orange $5UO_3,Na_2O$, $2NaHS$, and yellow $5UO_3,Na_2O$. In alkaline medium $5UO_3,Na_2O,2NaHS$ (orange) is transformed to $5UO_3,Na_2O$, $NaHS,Na_2S$ (red). H_2S converts the red to the orange.
          C. O. C.

Fluorescence and Photochemical Activity of Zinc Oxides. G. Winter and R. N. Whittem. *Australia, Dept. Supply and Develop.*, *Paint Notes*, **4**, 252–261 (1949): *Chem. Abs.*, **44**, 1719 (25th Feb. 1950).

A study of the relationship of these properties to the severe early chalking of paints containing ZnO. C. O. C.

PATENTS

2:8-Dihydroxynaphthalene-6-sulphonic Acid as the Azo Component for Diazotype Prints. W. H. von Glahn, L. N. Stanley, and General Aniline & Film Corpn.   *U.S.P.* 2,487,034.

Dark to reddish blue diazotype prints are obtained by using a diazotised *p*-phenylenediamine, e.g. *N*-phenylaniline-*p*-diazonium acid sulphate, and 2:8-dihydroxynaphthalene-6-sulphonic acid.   C. O. C.

Azo Coupling Components for Diazotype Materials. General Aniline & Film Corpn. and S. C. Slifkin.
          B.P. 634,341.

Compounds of formula $XO\cdot R(OH)\cdot CH_2\cdot SO_3H$ (R = a phenyl or naphthyl radical in which one coupling position adjacent or *para* to an OH group is open; X = H, acyl, alkyl, hydroxyalkyl, aryl, hydroxyaryl, or alkaryl) produce deep colours, have good solubility and no excessive coupling potential, and yield couplings which are waterfast and of good light fastness.   C. O. C.

4-Halogenoresorcinol as Coupling Component in Diazotype Layers. W. H. von Glahn, L. N. Stanley, and General Aniline & Film Corpn. *U.S.P.* 2,490,605.

4-Bromo(or iodo or fluoro)resorcinol gives a deep sepia colour when used as the coupling component in diazotype printing.   C. O. C.

Cyanine Dye Intermediates. E. B. Knott and Eastman Kodak Co.   *U.S.P.* 2,487,882.

β-Anilinovinyl derivatives of heterocyclic nitrogen compounds can be obtained directly in high yield and of high purity by heating a quaternary salt of a heterocyclic nitrogen compound having at least one reactive alkyl group with an alkyl*iso*formanilide. Thus 2-β-anilinovinylpyridine methiodide is obtained by refluxing a mixture of α-picoline metho-*p*-toluenesulphonate, methyl*iso*formanilide, and *n*-amyl alcohol and pouring the reaction mixture into aqueous potassium iodide.   C. O. C.
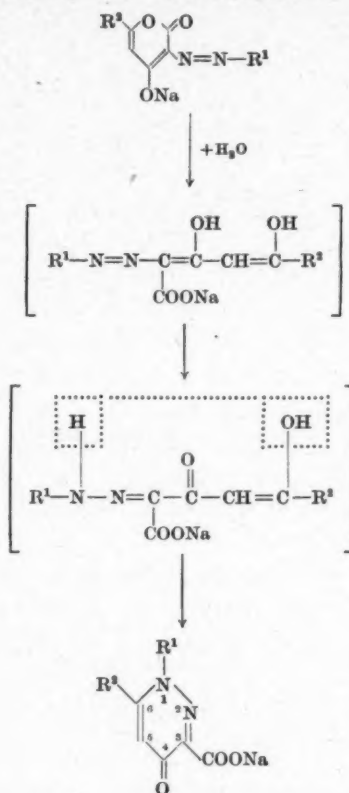
Polymeric Colour Formers. E. L. Martin and Du Pont.   *U.S.P.* 2,489,655.

Acetals of polymers containing several recurring intralinear $-CH_2\cdot CH(OH)-$ groups, especially those from *m*-(3-methylsalicylamido)benzaldehyde, give blue-greens on development with *p*-phenylenediamine-type developers. Coupled with aromatic diazonium salts the products are useful as pigments or in the surface coloration of textile fibres.   C. O. C.

Pyridazones from Azopyronones. J. F. Morgan and General Aniline & Film Corpn. *B.P.* 634,236.

4-Pyridazones substituted in the 1-position by aryl, in the 6-position by alkyl, aralkyl, or aryl, and in the 3-position by COOH are prepared by heating azopyronones

in water containing an alkali and a solvent miscible with water; rearrangement may be represented—

$$R^2\text{—C(O)(O)—C(ONa)}=N-N-R^1$$

$$+H_2O \downarrow$$

$$\left[R^1-N=N-C(COONa)=C(OH)-CH=C(OH)-R^2 \right]$$

$$\left[R^1-N-N=C(COONa)-C(O)-CH=C-R^2 \right]$$

$$\downarrow$$

(pyridazone structure with R^1, R^2, COONa)

(R^1 = aryl, free from sulpho groups; R^2 = alkyl, aralkyl, or aryl). Thus the yellow azo compound where R^1 = p-nitrophenyl and R^2 = CH_3 is refluxed with aqueous alcoholic sodium hydroxide to yield 1-p-nitrophenyl-3-carboxy-6-methyl-4-pyridazone.   E. S.

Monoazo Dyes for Acetate Rayon. J. B. Dickey and Eastman Kodak Co.   *U.S.P.* 2,491,481.
Dyes of formula—

$$O_2N\text{—}(C_6H_3)(X)(CF_3)\text{—}N=N\text{—}(C_6H_3)(C_2H_5)\text{—}N(R^1)(R^2)$$
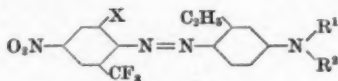
(R^1 = alkyl, hydroxyalkyl, alkoxyalkyl, cyanoalkyl, or carbalkoxyalkyl; R^2 = hydroxyalkyl; X = H, Hal, or CF_3) give dyeings of excellent dischargeability, excellent fastness to light and gas fading, and good fastness to washing and perspiration on acetate rayon, wool, silk, nylon, and vinyl acetate–vinyl chloride copolymers.
  C. O. C.

Red Azo Dye for Red Smoke Composition. J. Vinton and D. M. MacMillan.   *U.S.P.* 2,489,549.
The red dye—

$$H_3C\text{—}(C_6H_3)(CH_3)\text{—}N=N\text{—}(naphthol-OH)$$
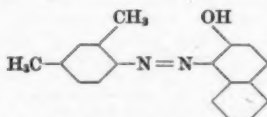
forms the principal component (13 parts by weight) of a red smoke which is clearly visible at a considerable distance even in the brightest daylight, the other components being Rhodamine B (1–3), lactose (8·5), and $KClO_3$ (7·0).
  C. O. C.

Blue Azo Dyes for Writing Inks. W. B. Reynolds and Parker Pen Co.   *U.S.P.* 2,489,463.
Blue dyes stable in aqueous caustic alkali have the formula—

(structure with H_2N, OH, X^1, X^2, SO_3Na, R^1, R^2, Y, SO_3Na, X^2, X^1, OH NH_2, N=N linkages)
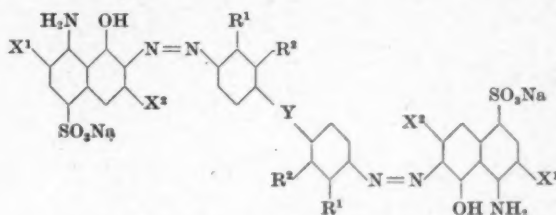
(X^1 = H when X^2 = SO_3Na and *vice versa*; when R^1 = H then R^2 = SO_3Na and Y = –CH:CH–; when R^1 = Cl then R^2 = H and Y = a single bond). They are obtained by coupling in alkaline solution 2 mol. of 1-amino-8-naphthol-2:4(or 4:6)-disulphonic acid with 1 mol. of 4 : 4′- diaminostilbene - 2 : 2′- disulphonic acid· or 3 : 3′-dichlorobenzidine. Dissolved in aqueous caustic alkali they yield stable blue writing inks.   C. O. C.

Monoazo Chrome Dye. H. W. Grimmel, L. Richter, and General Aniline & Film Corpn.   *U.S.P.* 2,487,540.
The monoazo dye 6-nitro-2-aminophenol-4-sulphonic acid→1-phthaloylamino-7-naphthol (alkaline coupling), dyed metachrome on wool, gives a bright green which does not change to any appreciable extent when viewed under artificial light. Dyed afterchrome it gives an olive black on wool without staining acetate rayon effects.   E. S.

**Yellow, Substantive, Disazo Dyes.** Ciba Ltd.
  B.P. 633,790.
Disazo dyes of formula $R^1\cdot N:N\cdot R^2\cdot NH\cdot CO\cdot R^3\cdot N:N\cdot Py$ (R^1 = the residue of a hydroxybenzoic acid; R^2 = a benzene or naphthalene residue in which the azo link and the –NH– group are not *ortho* to each other; R^3 = a benzene residue in which the –CO– group and the azo link are not *ortho* to each other; Py = the residue of a 5-pyrazolone, free from amino groups, which is bound in the 4-position to the azo link and contains a hydrocarbon radical in the 3-position) are yellow to yellow–orange substantive dyes, which may be metallised (e.g. with copper salts) on the fibre, and are generally dischargeable. Thus the dye —

(structure with HOOC, HO, HO_3S, N=N, N=N–C, pyrazolone ring with CH_3, HN—CO)
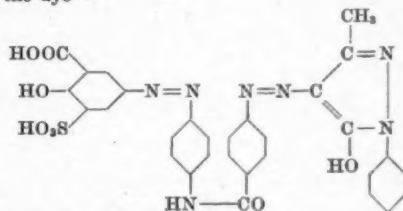
gives dischargeable greenish yellows on cotton.
  B.P. 634,130.
Disazo dyes of formula—

$$R^1\cdot N:N\cdot R^2\cdot NH\cdot CO\cdot NH\text{—}(C_6H_4)\text{—}N=N\text{—}(C_6H_3)(COOH)(OH)$$
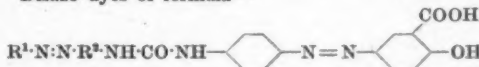
(R^1 = a naphthalene residue attached to the azo group in an α-position and containing at least one –SO_3H group but no auxochromic groups; –$R^2\cdot NH$ = the residue of an amine of the benzene or naphthalene series coupled *para* to the amino group) usually yield pure whites with neutral and alkaline discharges, unlike the similar products described in *U.S.P.* 1,594,828 and 1,781,682, where R^1 and R^3 are residues of the benzene series, which do not give satisfactory alkaline discharges. They are made by treating a mixture of two appropriate aminoazo compounds with phosgene. Thus the aminoazo compound 1-naphthylamine-3:6-disulphonic acid→cresidine is mixed with 4-amino-4′-hydroxyazobenzene-3′-carboxylic acid and treated with phosgene in presence of soda ash to yield an orange–yellow substantive dye, of good dischargeability.
  E. S.

Hydroxy Derivatives of Fuchsone and Fuchsone-imonium Dyes in a Direct Positive Photographic Process. R. E. Stauffer, J. Spence, and Eastman Kodak Co.   *U.S.P.* 2,490,758.

Naphthaquinoneimine Derivatives — Wool Dyes. Sandoz Ltd.   *B.P.* 633,663.
Red and violet to blue dyes for animal fibres, of general formula—
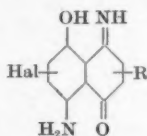
(R = radical of a water-soluble aromatic amine) are made by condensing a halogenated naphthaquinoneimine, prepared as described in *B.P.* 606,008 and 629,706 (J.S.D.C., **65**, 33 (Jan. 1949); **66**, 156 (Feb. 1950)) with the sulphonic or carboxylic acid of an amine of the benzene or naphthalene series. Thus brominated 5-amino-8-hydroxy-1:4-naphthaquinone (containing 44·6% Br and 7·9% N) is refluxed in aqueous *iso*propanol with sulphanilic acid and sodium acetate until a sample is soluble in water. The *iso*propanol is distilled off, and the product salted out.
     R. K. F.

Sulphuric Esters of Leuco Vat Dyes. S. Coffey, D. A. W. Fairweather, and I.C.I. Ltd.   *B.P.* 633,480.
1 : 4 - Di - (*p* - methanesulphonylbenzoylamino)anthraquinone in the form of a metal salt of its leuco compound is treated in presence of an organic amide derived from a secondary base, e.g. dimethylformamide, with a substance capable of forming sulphuric esters, e.g. sulphur trioxide or an addition compound of sulphur trioxide with an organic amide or tertiary base. Thus 1:4-di-(*p*-methanesulphonylbenzoylamino)anthraquinone is heated at 60–80°c. for 15 min. with potassium methyl sulphate, zinc dust, and dimethylformamide in an atmosphere of nitrogen. After cooling to 0°c. a solution of sulphur trioxide in dimethylformamide is added, and the temperature allowed to rise to 10°c. for 30 min. The leuco sulphuric ester is isolated by pouring into aqueous sodium carbonate and salting.

S. Coffey, D. A. W. Fairweather, D. E. Hathway, and I.C.I. Ltd.   *B.P.* 633,481.
Vat dyes and anthraquinone intermediates are converted to their leuco sulphuric esters by similar methods involving the use of organic amides.

S. Coffey, D. A. W. Fairweather, D. E. Hathway, F. H. Slinger, and I.C.I. Ltd.   *B.P.* 633,483.
The use of organic amides is extended to vat dyes consisting of carbazoles containing > 1 anthraquinone nucleus and at least 1 benzoylamino group per mol.

S. Coffey, D. A. W. Fairweather, F. H. Slinger, and I.C.I. Ltd.   *B.P.* 633,484.
Similar methods are used to make the sulphuric ester of leuco 1-benzoylamino-4-*p*-methanesulphonylbenzoylaminoanthraquinone.

S. Coffey, D. A. W. Fairweather, F. H. Slinger, and I.C.I. Ltd.   *B.P.* 633,485.
The sulphuric ester of leuco 1:1′:5:1″-trianthrimide-2:2′:6:2″-carbazole is prepared by similar methods.

S. Coffey, D. A. W. Fairweather, D. E. Hathway, and I.C.I. Ltd.   *B.P.* 633,486.
The methods are applied to vat dyes in which two anthraquinone nuclei are linked at their α-positions by the group –NH·CO·R·CO·NH– (–CO·R·CO– = the radical of a dibasic acid, e.g. terephthaloyl).
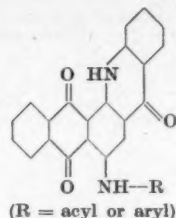
D. G. Wilkinson and I.C.I. Ltd.   *B.P.* 633,487.
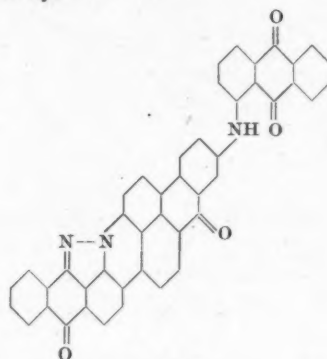Sulphuric esters of leuco thioindigoid dyes are prepared by similar methods.

D. A. W. Fairweather, F. H. Slinger, and I.C.I. Ltd.   *B.P.* 633,501.
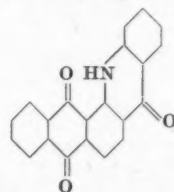Similar methods are applied to phthaloylacridone dyes of general formula—

(R = acyl or aryl).

F. H. Slinger and I.C.I. Ltd.   *B.P.* 633,502.
The vat dye—

is converted to its leuco sulphuric ester by similar methods.
D. A. W. Fairweather and I.C.I. Ltd.   *B.P.* 633,504.
Similar methods are applied to di- and tri-chloro derivatives of 1:2-phthaloylacridone—

D. A. W. Fairweather and I.C.I. Ltd.   *B.P.* 633,505.
Similar methods are applied to the vat dye—

     R. K .F.
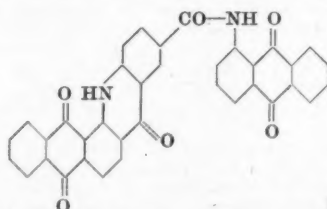
Sulphuric Esters of Leuco Vat Dyes. A. C. Robson, F. H. Slinger, and I.C.I. Ltd.   *B.P.* 633,492.
Vat dyes and anthraquinone intermediates are converted to their leuco sulphuric esters by first reducing in a suitable diluent, e.g. chlorobenzene, with a metal, e.g. zinc, powder and a primary or secondary amine capable of giving a blue co-ordination compound with copper hydroxide, e.g. methylamine. A catalyst, e.g. sodium β-naphthalenesulphonate, may be present. A sulphating agent, e.g. an addition compound of sulphur trioxide and an organic amide derived from a secondary amine, is then added. Thus dimethoxybenzanthrone is treated with zinc dust, sodium β-naphthalenesulphonate, dimethylformamide, and diethanolamine for 1 hr. at 80°c. under nitrogen. Dimethylformamide–sulphur trioxide (containing 40% SO₃) is next added at 0°c. The leuco sulphuric ester is isolated by pouring into sodium carbonate, filtering, and salting the filtrate.

F. H. Slinger and I.C.I. Ltd.   *B.P.* 633,498.
The method is applied to amino derivatives of dibenz-anthrone, prepared by treating dibenzanthrone with hydroxylamine.

F. H. Slinger and I.C.I. Ltd.   *B.P.* 633,499.
Mixtures of dihalogenoanthanthrones, e.g. dibromo-anthanthrone and bromoiodoanthanthrone, are converted to leuco sulphuric esters by similar methods. The products are dried with an alkali-metal carbonate.

S. Coffey, D. A. W. Fairweather, D. E. Hathway, and I.C.I. Ltd.   *B.P.* 633,493.
The leuco derivative of a vat dye or intermediate is converted to its sulphuric ester by treating with an organic amide–sulphur trioxide compound in presence of a nitrogenous base of dissociation constant $> 10^{-7}$ at $25°$c., e.g. *iso*propylamine.

S. Coffey, G. W. Driver, D. A. W. Fairweather, F. Irving, and I.C.I. Ltd.   *B.P.* 633,513.
The organic amide is replaced by a sulphonamide derived from a secondary amine, e.g. *NN*-diethyl-*p*-toluenesulphonamide.   R. K. F.

Symmetrical Carbocyanine Dyes. E. B. Knott and Eastman Kodak Co.   *U.S.P.* 2,487,881.
Symmetrical carbocyanine dyes can be made by condensing a quaternary salt of a heterocyclic nitrogen compound, having a methyl group attached to the C atom in the 2- or 4-position to the quaternary N atom, with formamide, thioformamide, thioformanilide, or formamidoxime. Thus the red dye 3:3'-dimethylthiocarbocyanine iodide—
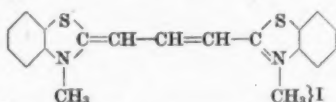

is obtained in 66% yield by refluxing 2-methylbenzthiazole metho-*p*-toluenesulphonate (3·35 g.) with thioformamide (0·33 g.) dissolved in ethyl alcohol (30 c.c.) until dissolved, adding triethylamine (0·5 c.c.), and refluxing for 30 min. The solution is then poured into aqueous KI, and the dye separated and recrystallised from methanol.   C. O. C.

Dye Intermediates containing Thiazolidone Rings and *mero*Cyanine Dyes therefrom. J. D. Kendall, G. F. Davis, and Ilford Ltd.   *B.P.* 634,951.
The compounds of formula—
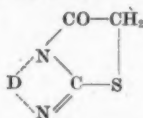
(D = residue of a 5- or 6-membered ring system), obtained by heating compounds of formula—
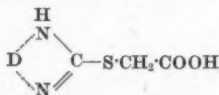
in presence of a dehydrating solvent, are useful as dye intermediates.
     B.P. 634,952.
*mero*Cyanine dyes are obtained when the above intermediates are combined with an alkyl or aralkyl quaternary salt of a 5- or 6-membered heterocyclic nitrogen compound containing in a or γ position to the quaternary N a thio-ether, selenoether, or vinyl-type group.   C. O. C.

Copper Phthalocyanine Dyes. G. M. O'Neal.
     B.P. 633,713.
Copper phthalocyanine dyes are made by heating together at 135–300°c. diammonium phthalate (or a derivative thereof formed by removing the elements of ammonia or water, e.g. phthalimide), biuret, and a copper compound. Yields are improved by including as catalyst a compound of an element of Group V or VI of the Periodic Table. Thus biuret, phthalic anhydride, ammonium molybdate, and anhydrous cupric chloride are heated together at a final temperature of 185–190°c. The cooled

product is ground and extracted in turn with boiling aqueous sodium hydroxide and hydrochloric acid.
     R. K. F.

Rhodacyanine Dyes. A. W. Anish and General Aniline & Film Corpn.   *U.S.P.* 2,490,572.
Treatment of thioethers of *mero*cyanines with an aliphatic or substituted aliphatic compound containing a reactive methylene group yields a class of cyanines which have an additional chromophore which is unlike that found in rhodacarbocyanine dyes. They have a sensitising action for a wavelength shorter than in the case of *mero*cyanine dyes.   C. O. C.

Luminescent Calcium Tungstate. British Thomson-Houston Co. Ltd. and R. S. Wells.   *B.P.* 634,616.
Luminescent calcium tungstate is prepared by heating calcium sulphate with ammonium tungstate. Lead nitrate may be added to the mixture as an activator for use with ultra-violet radiation.   C. O. C.

Air-stable Copper Powder. H. H. Robertson Co.
     B.P. 634,399.
A wet friable cement copper or copper precipitate has most of its moisture content rapidly removed and is then simultaneously given an impacting treatment and flash-dried in an oxidising atmosphere, so that a very thin protective film of cuprous oxide is formed around each particle.   C. O. C.

Sublimed White Lead. E. C. Handwerk, G. T. Mahler, and New Jersey Zinc Co.   *U.S.P.* 2,488,398.
A process for producing sublimed white lead from argentiferous galena with subsequent recovery of silver and gold.   C. O. C.

Titanium Oxide Pigments. H. H. Schaumann and Du Pont.   *U.S.P.* 2,488,439
     U.S.P. 2,488,440.
Titanium oxide pigments are produced by the controlled oxidation of gaseous $TiCl_4$. The products have uniform particle size, and good contour, tinting strength, opacity, hiding power, etc., and can be obtained in either the rutile or anatase form.   C. O. C.

V— PAINTS; ENAMELS; INKS

PATENT

Flushing of Pigments. Lewis Berger & Sons Ltd.
     B.P. 634,835.
Non-aqueous dispersions of a pigment in a liquid or liquefiable organic vehicle are obtained by mixing an aqueous mixture or dispersion of the pigment with the vehicle in presence of benzylamine or an *N*-substituted methyl or benzyl derivative thereof.   C. O. C.

Wrinkle-drying Compositions containing Dextran Derivatives. E. L. Luáces and New Wrinkle Inc. (III, p. 332.)

Titanium Dioxide Pigments. A. E. Jacobsen. (IV, p. 334.)

Blue Azo Dyes for Writing Inks. W. B. Reynolds and Parker Pen Co. (IV, p. 335.)

VI— FIBRES; YARNS; FABRICS

Chemistry of Incompletely Cleaned Cotton. M. M. Chilikin. *Tekstil Prom.*, 9, 20–22 (Nov. 1949).
An examination has been made of those materials arising from the cotton plant which are not rejected in the preliminary sorting processes of raw cotton, and contaminate the fabric as received by the finisher. Analyses were carried out for cellulose, lignin, wax, and nitrogen, and the loss in weight during a caustic soda boil was also determined. The materials examined were— the outer and inner walls of the boll, the fine hairs from the inside of the boll, the husk of the seed, and the leaf. In addition analyses were made of normal raw cotton, of neps, which often contain dead and immature cotton, of pieces of husk with attached hairs (motes), and of dead cotton. Neps, motes, and dead cotton all have high wax contents, particularly the last; the lignin content is also high, particularly for motes (11%). Portions of material containing these defects were dyed with dyes of various classes, viz. direct cotton, vat, soluble leuco-vat ester, sulphur, azoic. The fibres were then examined microscopically. The effect of mercerisation or a hypochlorite bleach prior to dyeing was also examined. The dyeing

properties of dead cotton were little affected by mercerisation and bleaching, and the proportion of well dyed fibres was much higher for the sulphur dyes than for the other classes. The dyeing of neps was improved by mercerisation; sulphur dyes gave the best results. The hairs attached to the motes did not dye so readily as normal cotton hairs. Even after mercerisation, bleached motes dyed very poorly, particularly with azoic dyes. A. E. S.

Density and Structure of Mechanically Modified Cellulose. E. Steurer and F. Katheder. *Kolloid-Z.*, 114, 78–88 (Aug. 1949).

Cellulose after grinding and recrystallisation shows loss in density, which then increases on subsequent wetting with water or heating to 180°c. The crystalline and amorphous contents of cotton and other celluloses before and after mechanical modification are calculated, and their relationship to the molecular structure of the fibre is discussed. B. K.

Submicroscopic Structure of Cellulose from Nitrogen-sorption Measurements. C. M. Hunt, R. L. Blaine, and J. W. Rowen. *Text. Research J.*, 20, 43–50 (Jan. 1950); *Bur. Stand. J. Res.*, 43, 547–554 (Dec. 1949).

When cotton linters are swollen with strong alkali and then given a solvent-exchange treatment, the material is found to have a large surface area available to nitrogen absorption. The absorption isotherms showed strong hysteresis. Pore size distributions showed that most of the nitrogen was absorbed in pores having radii of about 20A. The addition of 11% moisture destroyed nearly all of the internal surface, and the isotherm more closely resembled that of untreated cotton. Cotton swollen with water only and given a solvent-exchange treatment also had a much larger surface than untreated cotton. P. C.

Estimation of the Polymolecular Structure of Cellulose. H. A. Wannow. *Melliand Textilber.*, 30, 519–522 (Nov. 1949).

The distribution of the chain lengths of polymolecular cellulose is ascertained by ultracentrifugal dispersion analysis and fractionation by precipitation and redissolving. Details are given for preparing distribution diagrams of the chain lengths from the data obtained. It is shown, with the aid of the fractionation results found in cotton decomposed by oxidation, that distribution into eight fractions is sufficient to secure an exact distribution diagram. B. K.

Cellulose Studies. XIII— Heterogeneous Hydrolysis of Trimethyl Cellulose. R. Steele and E. Pacsu. *Text. Research J.*, 19, 771–793 (Dec. 1949); 20, 42 (Jan. 1950).

Structure of the Jute Fibre. II— The Rôle of the Lignin–Hemicellulose Complex and other Noncellulosic Constituents. M. K. Sen and P. H. Hermans. *Rec. Trav. chim.*, 68, 1079–1105 (Dec. 1949).

Swelling measurements, staining of cross-sections, and the study of X-ray diagrams taken with monochromatic radiation, combined with previous knowledge (cf. *Biochim. et Biophys. Acta*, 3, 510 (1949); *Nature*, 161, 768 (1948)), indicate that—(1) The lignin is not uniformly bound. The relatively small fraction most difficult to remove is located in the outer layers of the fibre beyond the secondary wall, and plays a part in the structure, acting as a barrier to swelling. This barrier is probably associated with the middle lamella, since swelling becomes normal if the middle lamella is damaged (2) The optical observations show that the birefringence of the outermost cell layers (primary wall) persists through all purification operations. (3) The X-ray data also show that the crystalline cellulose in the jute fibre remains the same in quantity throughout the purification operations, and bears the same ratio to the total cellulose as in ramie, cotton, and flax. H. H. H.

Some Replica Techniques useful in Electron Microscopy of the Surface of the Wool Fibre. K. R. Makinson. *Text. Research J.*, 20, 22–28 (Jan. 1950).

Various replica techniques are described which have been developed for making an examination of the surface structure of the wool fibre in the electron microscope. Photographs are reproduced to illustrate the appearance of normal wool fibres and of fibres subjected to chemical and mechanical treatments. P. C.

Note on the Disintegration of Wool in Abrasion Tests. H. F. Schiefer and J. F. Krasny. *Text. Research J.*, 19, 802–809 (Dec. 1949); *Bur. Stand. J. Res.*, 44, 9–14 (Jan. 1950).

When a wool fabric is abraded on the Schiefer abrasion machine, the abrading surface becomes coated with a substance which causes the rate of abrasion to increase appreciably. A critical examination of this material showed it to consist of extremely small spherically shaped particles of 100–200A. in size, and having the same infrared absorption characteristics and chemical analysis as the unabraded fabric. It is concluded that the coating consists of extremely small particles of wool, which appear to correspond in shape and size to the elemental structural units proposed in recent concepts of the structure of wool. P. C.

Softening Temperatures of Various Fibrous Keratins. H. Zahn. *Kolloid-Z.*, 114, 123 (Aug. 1949).

Correction to previous paper, *ibid.*, 113, 157–159 (June 1949) (cf. J.S.D.C., 66, 79 (Jan. 1950)).

Hygroscopic and Wetting-out Properties of Keratins. O. Jacobi. *Kolloid-Z.*, 114, 88–103 (Aug. 1949); 116, 48 (Jan. 1950).
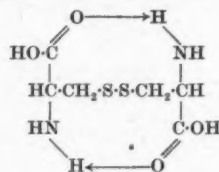
Experiments have shown that keratins, both untreated and degreased with fat solvents, are hydrophilic (i.e. they can be wetted out) and are also hygroscopic. Horn substances impregnated with keratin fats are, however, hydrophobic (i.e. do not wet out), but nevertheless are hygroscopic. Keratins extracted with water or alcohol, or water or alcohol followed by ether, are hydrophobic but hygroscopic. Horn substances, however, impregnated with water or alcohol extracts are hydrophilic. B. K.

Products of the Hydrolysis of Wool Keratin by Papain. S. Blackburn. *Nature*, 165, 316–317 (25th Feb. 1950).

Previous work by Middlebrook and Phillips (J.S.D.C., 57, 137 (1941)) is now extended to the hydrolysis products themselves, when wool is treated with 2% papain for 3½ hr. at 65°c. in 1% sodium bisulphite solution. The peptide precipitated by acidification to pH 4 has a disordered β-keratin type of structure and has a fairly long chain-length, while the peptides in soln. have a mean chain-length of 5 amino acid residues, and a two-dimensional chromatogram in collidine and phenol–ammonia showed glycine but no appreciable amount of other free amino acids. The following terminal amino acids were found among the peptides— leucine + isoleucine, valine, alanine, glycine, threonine, serine, and glutamic and aspartic acids. The enzyme thus liberates a large number of different amino groups from the peptide linkages, but with no high degree of specificity in its action on wool. H. H. H.

Anomalous Rotatory Power of Cystine. L. F. Fieser. *Rec. Trav. chim.*, 69, 410–415 (March 1950).

To explain the remarkably high optical rotatory power of cystine, $[a]_D - 214°$, cited originally by van't Hoff, the author has proposed the structural formula—

$$\begin{array}{ccc} & O \longrightarrow H & \\ HO \cdot C & & NH \\ HC \cdot CH_2 \cdot S \cdot S \cdot CH_2 \cdot CH & \\ HN & & C \cdot OH \\ & H \longleftarrow O & \end{array}$$

based on the Mirsky and Pauling postulate (*Proc. Nat. Acad. Sci.*, 22, 439 (1936)) for the structure and properties of native proteins. H. H. H.

Unstable Lattice in Silk Fibroin. O. Kratky, E. Schauenstein, and A. Sekora. *Nature*, 165, 319–320 (25th Feb. 1950).

Brill's X-ray experiments (*Liebigs Annalen*, 434, 204 (1923)) on dried silk fibroin have been repeated, and the fibroin, present in the native silk gland in a dispersed state, has been found to form crystals on drying which are much larger than those of the spun silk fibroin. The facile transition to the well known β-diagram, however, has prevented determination of the orientation of the primarily formed crystallites for measurement of the fibre period. An X-ray photograph perpendicular to the plane of stretched

fibroin micelles shows the remarkable effect of a faint double structure, viz. with the chain directions parallel and perpendicular to the direction of stretching (after swelling in formic acid). Changes are ascribed to the formation of $C=N$ links within the peptide chains by transition of $-CO\cdot NH-$ to $-C(OH){:}N-$.   H. H. H.

X-Ray Investigation of Dissolved Fibre Molecules.
O. Kratky and G. Porod. *Rec. Trav. chim.*, **68**, 1106–1122 (Dec. 1949).

By a detailed mathematical discussion of the X-ray scattering curve of chain molecules in solution, four regions are distinguished, due to— (1) the diffraction effect of the whole coiled chain molecule; (2) that of parts of the chain molecule; (3) the scattering of mostly straight parts of the molecule; and (4) the smaller parts of the molecule, this providing a measure of its coiling. Measurements with polyvinyl bromide lead to a length of persistence of 11 ± 1 A., which agrees satisfactorily with the value of 13A. for polyvinyl chloride derived from the birefringence of flow. Measurements with cellulose nitrate indicate a chain-element longer than 150 A., in agreement with results from other data. The procedure is claimed to be superior to other methods for a direct evaluation of the shape of chain molecules.   H. H. H.

Estimation of the Crystalline Portion of Macromolecular Synthetic Fibres.
A. Sippel. *Kolloid-Z.*, **114**, 123 (Aug. 1949).

Correction to previous paper, *ibid.*, **113**, 74–82 (May 1949) (cf. J.S.D.C., **66**, 80 (Jan. 1950)).

Filtration of Viscose and its Influence upon the Stress–Strain Properties of Isotropic Xanthate Filaments.
H. L. Vosters. *Svensk Papperstidning*, **53**, 29–34, 59–64 (31st Jan., 15th Feb. 1950).

Structural Viscosity of Viscose.
A. Lude. *Rec. Trav. chim.*, **68**, 1030–1036 (Dec. 1949).

A series of tests on different viscoses under tensions ranging from 10 to 400,000 dynes/sq. cm. has enabled the influence of the following factors on structural viscosity to be determined— average chain length, concentration of cellulose, soda content, and degree of maturity of the viscose; the most important factor is found to be the first-named.   H. H. H.

Preparation and Properties of Alkali-soluble Metal Carboxymethylcellulose Fibres.
J. D. Reid and G. C. Daul. *Text. Research J.*, **19**, 794–801 (Dec. 1949).

Metal carboxymethyl cellulose fibres have been produced on a pilot-size spinning machine from sodium carboxymethyl cellulose and metals capable of cross-linking. Fibres with strengths of 1–2 g./grex can be obtained, and an aluminium–copper carboxymethyl cellulose fibre has the best combination of physical properties such as strength, appearance, flexibility, and handle. The fibres appear to have no unique shape of cross-section, which is probably controlled mainly by conditions of extrusion, coagulation, and drying. The average diameter of the fibres is of the order of 0·027 mm. The fibre is similar in characteristics to alginic acid fibres, and should be of interest in applications requiring an alkali-soluble fibre.   P. C.

Synthesis of Disulphide Cross Links in Polyvinyl Alcohol and Cellulose Derivatives.
E. F. Izard and P. W. Morgan. *Ind. Eng. Chem.*, **41**, 617–621 (March 1949).

Cross-linkages, incorporating the disulphide group, have been introduced into polyvinyl alcohol and cellulose by treatment of their chloroacetyl esters with sodium thiosulphate, followed by mild oxidation or treatment with formaldehyde. Disulphide cross-links, attached directly to the polymer chain, have been synthesised in cellulose esters by reaction of the substituent *p*-tosyl groups with sodium thiosulphate, thiourea, or pyridine and hydrogen sulphide, followed by oxidising aftertreatments. The products in the form of films or fibres are insoluble in organic solvents, and do not fuse below their decomposition points. Presence of the disulphide linkage was demonstrated, with the exception of the (methylenedithio)-diacetyl link, by reduction of the cross-linked polymers to the soluble thiol form with thioglycollic acid, followed by reoxidation to insoluble disulphide. These cross-linking reactions were very mild, so that little polymer degradation occurred. Sulphur analyses showed that degrees of cross-

linking as high as one link per five anhydroglucose units did not give embrittlement.   G. L.

Influence of Hemicellulose Content on the Acetylation of Cellulose.
G. Jayme and U. Schenck. *Melliand Textilber.*, **31**, 153–156 (March 1950).

Regenerated Keratin Fibres from Wool.
F. Happey and R. L. Wormell. *J. Textile Inst.*, **40**, T 855–T 869 (Dec. 1949).

Methods are described by which wool is dispersed and extruded into a continuous-filament yarn with a β-keratin structure. The wool is dissolved by cold digestion with sodium sulphide solution, reprecipitated, redissolved, refined in cuprammonium, and again reprecipitated. Finally an approx. 35% solution of the wet curd is made in either cupramonium or ammonia, and after filtration, the yarn is spun into a salt bath, and stretched and hardened in two stages. The tenacity and extension of the final yarn are respectively 1 g./denier and 30% at normal condition and 0·3 g./denier and 33% wet. The stretching and hardening greatly improve the yarn properties, and X-ray photographs show that there is an increase in the crystallinity of the β-keratin which may be carried almost to the limit by stretching the finished yarns in steam. It is suggested that the process provides a means of regenerating a continuous-filament β-keratin yarn from waste wool and other α-keratin proteins.   W. K. R.

PATENTS

Aftertreatment of Viscose Rayon Packages.
J. W. Jacokes and American Enka Corpn. *U.S.P. 2,488,667.*

Formation of dark spots at the surface of the packages is prevented by treating them with a special alkali or salt solution between washing free from acid and desulphurising.   C. O. C.

Threads of Cyanoethyl Ethers of Cellulose.
Courtaulds Ltd., J. H. MacGregor, and C. Pugh. *B.P. 633,807.*

Yarn which can be used as carrier threads is made by extruding an alkaline solution of cyanoethyl ethers of cellulose, prepared by treating viscose with 0·5–1·2 mol. of acrylcnitrile per mol. of cellulose, into an acid coagulating bath.   W. G. C.

Interpolyamides.
J. G. N. Drewitt and G. F. Harding. *B.P. 632,997.*

Fibres of high m.p. can be spun from interpolymers of an aliphatic dicarboxylic acid with 5–15% of an aromatic diamine, whose *NN'*-diacetyl derivative melts at not < 270°c., and 85–95% of an aliphatic diamine.   W. G. C.

Strengthening Polymeric Materials.
Du Pont. *B.P. 634,600.*

A normally solid polymer of polyethylene, polyvinylidene chloride, an interpolymer of ethylene with other polymerisable compounds wherein the proportion of ethylene is > 60% by wt., or an interpolymer of vinylidene chloride with other polymerisable compounds wherein the proportion of vinylidene chloride is > 80% by wt. is greatly strengthened by cold-drawing under tension applied at an angle > 30° to the original orientation, which must already be substantial.   J. W. B.

Linear Polyvinylacetals.
C. W. Gayler and American Viscose Corpn. *U.S.P. 2,487,864.*

Polyvinylacetals having no cross-links between chains and so suitable for making into fibres which can be stretched are obtained by treating an aldehyde, e.g. $H\cdot CHO$, with a polyvinyl alcohol suspended in a liquid which is a solvent for the resulting acetal and for the water produced during the condensation but which is a non-solvent for the alcohol. The time of treatment is 20–30 min., and the treatment is carried out in absence of external heat and pressure.   C. O. C.

Conditioning or Lubricating Carded Fibres.
Monsanto Chemical Co.   *B.P. 634,125.*

Carded fibres are partly condensed as they leave the card and are then treated on both sides of the web with finely divided liquid before being condensed to a sliver. The method is particularly suitable for applying colloidal silica to cotton, as complete penetration is obtained without any tendency for the silica to congeal or gum up on the fibre. Suitable apparatus is described.   C. O. C.

The Superpolyurethanes.
M. Souvé. (XIII, p. 342.)

Production of Polyesters.
J. G. N. Drewitt and J. Lincoln. (XIII, p. 343.)

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VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Pad–Steam Scouring Process. A. V. Surovaya. *Tekstil. Prom.*, 9, 29–31 (Oct. 1949); 22–24 (Nov. 1949).

The method of scouring cotton fabrics prior to bleaching by padding in a solution of caustic alkali and steaming was devised in 1888 by a Russian, P. I. Lukyanov. The method is very effective in removing impurities, but very frequently motes are incompletely destroyed. In the present investigation conditions for a satisfactory scour have been established for a number of fabrics varying in openness of weave and twist of yarn. A hypochlorite bleach following such a treatment yielded a fabric which was not inferior to fabric treated by the classical kier-boil–hypochlorite bleach as regards freedom from motes, whiteness, and physicochemical properties such as absorbency and cuprammonium viscosity. The treatments were carried out on sized and desized cotton fabrics, cotton in the form of roving, and also, in some cases, on cottonseed husks, which were held in a bag of cotton fabric during treatment. The material was impregnated at 40°c. in a solution of caustic soda, varying in concn. from 0·25 to 10%, and in some experiments additions were made of surface-active agents (including oleylmethyltaurine, an alkyl-naphthalenesulphonic acid, and a sulphonated primary alcohol), and/or of oxidising agents (Chloramine B, sodium chlorite, and sodium hypochlorite). The material was then squeezed, so as to leave 100% on its weight of residual solution, and was steamed at atmospheric pressure for 10–120 min. It was washed in water, steeped for one hour in cold dilute acetic acid, rinsed, and dried. Measurements were made of loss in weight, turbidity of solution in concn. sulphuric acid, content of pectic substances, rate of dyeing with a direct cotton dye, absorbency, tensile strength, and cuprammonium viscosity. A concn. of 3–4% caustic soda was generally required to give good absorbency in a one-hour steam. No appreciable degradation of cellulose occurred, even when the concn. was raised to 10%, or when additions of oxidising agents were made. The tensile strength of the product was in all cases greater than that obtained in a comparable kier treatment. The whiteness and absorbency of the final product were improved by additions of oxidising agents, but these had no effect on the removal of motes. The addition of certain surface-active substances led to increased whiteness and absorbency, and aided, to some extent, in the destruction of motes. It was found that the loss in weight of cottonseed husks was greatly increased by a steeping process prior to the alkaline impregnation. By applying such a process to a fabric it was possible to destroy the motes completely. In one recommended process the fabric was given a steep in dilute alkali, followed by a second steep in dilute acid, then rinsed, and given a pad–steam treatment. The final bleached fabric was in no respect inferior to fabric processed in the kier.   A. E. S.

[Crabbing and Steaming Preparatory to] the Dyeing of Dress Goods. *Wool Record*, 77, 813–817 (16th March 1950).

A detailed practical account of the crabbing and steaming of dress goods and particularly of the steps to be taken to prevent faults arising which would show up in subsequent dyeing.   C. O. C.

VIII— DYEING

Relation between Dye Absorption and Density of Cellulosic Fibres. E. Elöd and H. G. Frölich. *Melliand Textilber.*, 31, 179–182 (March 1950).

Some types of cellulose hydrate fibre possess a surface skin which has a higher density than the core of the fibre. The skin exerts a pronounced influence on the absorption of direct dyes. This has been proved by dye absorption measurements on different types of rayon. The fibres with the greatest difference in density between core and surface, i.e. those in which the skin effect was most pronounced, showed the lowest rate and extent of absorption of direct dyes. It is believed that the reduced size of the pores in the skin hinders access of dye to the fibre. F. A.

Dyeing with Azoic Dyes. W. Hees. *Melliand Textilber.*, 30, 359–363 (Aug. 1949); 30, 525–528 (Nov. 1949); and 31, 47–48 (Jan. 1950).

The optimum coupling conditions for each individual combination of naphthol and base are a function of their chemical constitutions, the base playing the more important part. The energy and speed of coupling are determined by the substituents in the molecule, and the amines can be classified into four groups in this respect. The optimum pH range for development of various azoic dyeings can be adjusted in practice by the method of neutralisation of the diazo soln., by suitable alkali-binding agents, as well as with suitable buffers, and is given in tabular form. Bases and salts are classified into four main groups as regards optimum pH range with respect to rate of coupling— high rate of coupling pH 4–5, moderate pH 5·5–6·5, slow pH 6–7, very slow pH 7–8·2. Details are given for the application of different combinations of naphthols and bases together with methods of development. The pH of the developing bath can be calculated theoretically by means of the following equations—

(1) $\quad \mathrm{pH} = 0{\cdot}5 \ \mathrm{p}K - 0{\cdot}5 \ \log C_1$

(2) $\quad \mathrm{pH} = \mathrm{p}K - \log C_1 + \log C_2$

(K = dissociation constant of acetic acid; C_1 and C_2 = concn. of acetic acid and sodium acetate respectively).   B. K.

Acid Leuco Vat Dyeing Process. J. Müller. *Melliand Textilber.*, 30, 364–368 (Aug. 1949).

A survey of the development and application of the acid leuco vat dyeing process, which started with the original observations of the I.G. on the acid leuco derivatives of Indanthren Blue RSN and GCD. The acid leuco compounds, in contrast to the sodium leuco compounds, have no affinity for the fibre, but are converted into the latter by treatment with NaOH. They are applicable by machine dyeing and various padding techniques, and exhibit certain advantages, e.g. improvement in levelness and penetration, and permit working at a high speed. Details of the application of these compounds by the Du Pont pad–steam, the Williams unit, and other processes are given.   B. K.

Vat Dyeing: Importance of Initial Exhaustion Rate. O. W. Clark and H. R. McCleary. *Amer. Dyestuff Rep.*, 38, P 828–P 832 (14th Nov. 1949).

A knowledge of the exhaustion behaviour of individual dyes enables dyes having similar characteristics to be used in mixtures, and promotes trouble-free dyehouse operation. The equilibrium exhaustion and "initial exhaustion rate" (percentage of total dye concentration exhausted per minute at the beginning of dyeing) of several vat dyes have been measured with the Dyeometer. As a result of continuous laboratory-scale dyeings it is concluded that initial exhaustion rates are more useful than equilibrium exhaustion data in predicting compatibility of dyes.   A. S. F.

Application of Carbolan Dyestuffs to Wool Yarn. H. Crook, D. R. Lemin, and I. D. Rattee. *Textile J. of Australia*, 24, 759–762, 764, 766–770, 772 (Oct. 1949).

The use of Glauber's salt and Carbolan Salt A as dyebath assistants enables Carbolan (ICI) dyes to be dyed more level, mainly because these assistants lead to a more even rate of dyeing and a considerably increased rate of boiling-off. This new dyeing technique will enable Carbolan dyes to be used where formerly it has only been possible to employ level-dyeing acid dyes. The new dyeing technique will not overcome unlevelness of shade arising from faulty scouring, presence of metal soaps, or variations in the wool fibre. On the basis of exhaustion experiments under various conditions, lists of dyes are recommended for application in full, medium, and pale shades. A. S. F.

General Theory of Chrome and Aluminium Mordants in the Dyeing of Wool. Dr. Justin-Mueller. *Teintex*, 15, 57–71 (Feb. 1950).

A detailed review of the subject is given in seven sections— (1) Chrome-mordanting of wool before dyeing; specific properties of dyes which enable fixation by mordants. (2) Aftertreatment by dichromate. (3) The effect of labile sulphur: theory of chrome-mordanting involving either sulphuric, tartaric, or formic acid; dyeing on the chrome mordant; the chromium–dye complex on wool; subsequent fixation; and the metachrome process. (4) Compounds with chromium hydroxide and fluoride;

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Dyeing Shoddy containing Vegetable Fibres. K. Wojatschek. *Melliand Textilber.*, **31**, 192–194 (March 1950).

Various one-bath methods for the dyeing of shoddy containing vegetable fibres and aftertreatments for obtaining improved fastness are described.   F. A.

Dyeing Mixed Acetate and Viscose Fabrics with Vat Colours. American Association of Textile Chemists and Colorists, Piedmont Section. *Amer. Dyestuff Rep.*, **38**, P 816–P 821 (14th Nov. 1949).

Solid shades can be obtained on acetate rayon–viscose rayon or cotton unions, without recourse to swelling agents or saponification, by dyeing with vat dyes in presence of tannic acid and Katanol W. The Katanol W increases the depth of shade on the acetate rayon and gives more level results than can be obtained with tannic acid alone. If Katanol W is used alone, the final dyeing tends to turn brown on exposure to light. With proper control, vat dyes can be applied in this way to acetate rayon with negligible saponification of the fibre, to give dyeings having very good fastness properties, particularly to gas-fume fading.   A. S. F.

PATENT

Continuous Pigment-padding Dyeing. P. H. Stott, R. A. Shimp, and Du Pont.   U.S.P. 2,487,197.

Cloth is padded with a very dilute aqueous suspension of a vat dye, passed through a reducing solution below the temperature at which the dye is reduced, and is then immediately passed into an air-free steam chamber, where the colour is reduced and fixed quickly at not $< 100°$c. It is then oxidised, soaped, etc. as usual. The process is very rapid and also economical in dyes and chemicals.
    C. O. C.

Practical Tests for Quantitatively Evaluating Dye Characteristics and Dyeing Methods. American Assocn. of Textile Chemists and Colorists, Northern New England Section. (XIV, p. 244)

IX— PRINTING

Sodium Alginate as a Thickener in Printing Pastes. E. K. H. Schmidt. *Melliand Textilber.*, **31**, 194–196 (March 1950).

Recommendations are made for the use of sodium alginate as a thickening agent in printing pastes, and recipes are given for different types of dye.   F. A.

PATENT

Electronograph Printing. W. C. Huebner.
    B.P. 634,278.

The ink on the printing surface is given an electrical precharge, and the material to be printed introduced into the printing zone, in which an electric field of force is then created so as to transfer the precharged ink from the printing surface to the material to be printed. This material must have been first rendered electrically neutral and then given an electrical precharge of predetermined polarity before it is introduced into the printing zone.
    C. O. C.

2:8-Dihydroxynaphthalene-6-sulphonic Acid as the Azo Component for Diazotype Prints. W. H. von Glahn, L. N. Stanley, and General Aniline & Film Corpn.   (IV, p. 334.)

X— SIZING AND FINISHING

Dimensional Changes occurring in Spun Viscose Rayon Fabrics during Processing on Machinery used in Shrinkage Stabilisation Finishing. American Association of Textile Chemists and Colorists, Philadelphia Section. *Amer. Dyestuff Rep.*, **38**, P 822–P 827 (14th Nov. 1949).

The dimensional changes occurring in the padding, stentering, curing, calendering, washing, and drying operations of shrinkage control by resin treatment are described, and suggestions are given for controlling the various processes adequately.   A. S. F.

Prevention of Supercontraction in Modified Wool Fibres. A. E. Brown, J. H. Pendergrass, and M. Harris. *Text. Research J.*, **20**, 51–52 (Jan. 1950).

The supercontraction properties of wool stabilised by treatment with hydrosulphite and ethylene dibromide have been determined, and it is found that such fibres supercontract less than 1% in bisulphite compared with 20% for untreated fibres. Fibres modified with sodium formaldehyde-sulphoxylate and methylene dibromide behaved similarly. Alkaline hydrosulphite is also an excellent supercontraction medium. It has also been found that the addition of ethylene dibromide to bisulphite solutions prevents supercontraction of wool in such a solution. All these results are evidence of the prominent rôle played by the disulphide bonds in supercontraction and setting phenomena.   P. C.

Supercontraction of Wool and Other Keratin Fibres in Phenol. H. Zahn. *Melliand Textilber.*, **30**, 517–519 (Nov. 1949).

Supercontraction of wool and related fibres has been found to be over 30% if the fibres are heated with highgrade phenol. The presence of a wide range of organic compounds has been found to diminish the supercontraction of horse-hair in phenol. Low-grade phenol can be purified by separating the neutral oils and the higherboiling fraction.   B. K.

Static in Textile Processing. D. J. Lehmicke. *Amer. Dyestuff. Rep.*, **38**, P 853–P 855, P 862 (28th Nov. 1949).

"Static" refers to the observable effects of the accumulation of electrostatic charge. Such effects are— sparking when the charged object is brought near a conductor, repulsion between adjacent filaments of yarn which has been passed over a guide, and attraction of light particles by a charged body. The positions of well known fibres in an electrostatic series is given, and the difficulties due to static in textile processing, together with their remedies, are pointed out.   A. S. F.

Drying of Cellulose Fibres. K. Lauer, O. Bezner, and O. Dobberstein. *Kolloid-Z.*, **116**, 28–31 (Jan. 1950).

Experiments on the drying of viscose have shown that increased drying temp. gives fibres of lower swelling value and decreased affinity for dyes. These properties are a measure of the magnitude of the internal surfaces and the length of the cross-linkages in the amorphous portions of the fibre. These changes are partly reversible. Prolonged drying or repeated drying and steaming lead fundamentally to the same results. The drying process leads to the formation of new cross-linkages in the amorphous regions, which account for such properties as swelling, brittleness, etc.   B. K.

Action of Acid Catalysts in the Drying of Cellulose Fibres. K. Lauer, O. Bezner, and O. Dobberstein. *Kolloid-Z.*, **116**, 31–33 (Jan. 1950).

Reversible and non-reversible cross-linkages are formed in the amorphous portions of viscose on drying. A new kind of bridge formation is, however, observed when drying in the presence of acid catalysts, which is shown by a decrease in the solubility in cuprammonium soln.
    B. K.

Incidence and Control of Mildew on Textiles. M. Nopitsch. *Melliand Textilber.*, **31**, 182–188 (March 1950).

The conditions which favour growth of mildew on textiles are detailed. The main types of fungi which are responsible for damage are then described, and their appearance is illustrated by photomicrographs. The variety of proofing agents which are available is described with emphasis on the heavy-metal salts of phenolic-type antiseptics.   F. A.

Effect of Copper Salts on the Fastness of Vat Dyeings. J. P. Niederhauser. *Teintex*, **15**, 109–123 (March 1950).

Treatment with copper salts for rotproofing cotton gives an excellent protection in the absence of actinic rays. The author's investigations with Solanthrene (Fr) and other vat dyes have shown that the presence of copper exerts a markedly deteriorating effect on the fastness to

light of vat dyes and also causes tendering of the cotton on exposure to sunlight.   B. K.

Urea–Phosphoric Acid Method of Flameproofing Textiles. F. V. Davis, J. Findlay, and E. Rogers. *J. Textile Inst.*, **40**, T 839–T 854 (Dec. 1949).

It has been confirmed that a flameproof finish fast to hot water and mild laundering is imparted to cotton fabrics by treatment with a mixture of urea and phosphoric acid followed by baking at 130°–175°c. The flameproofing efficiency depends on the phosphorus content of the treated material, at least 3% being necessary for complete flame resistance; such treatment involves a loss in strength of about 20%. The phosphorus is firmly bound and associated with nitrogen present as the ammonium radical, the latter being easily removed by alkali. Repeated alkaline washing causes some diminution of the flame resistance, but does not reduce the phosphorus content, and the original flameproof is restored by acid treatment. Evidence is presented which indicates that the flame resistance is due to surface esterification of the cotton, the ammonium salt of cellulose-orthophosphoric acid being formed. Heating urea and orthophosphoric acid alone at the baking temp., however, results in the formation of diammonium pyrophosphate and cyanuric acid; the former is assumed to be the esterifying agent. Treatment of cotton with diammonium pyrophosphate gives negligible flame resistance, and it appears that the presence of excess urea is necessary as a medium to secure the fixation of > 3% phosphorus without great loss of strength, an effect which is not otherwise attainable.   W. K. R.

PATENT

Adhesion of Rubber to Cellulosic Fibrous Materials. F. S. Perkerson and Callaway Mills Co.
    U.S.P. 2,486,720.

Better adhesion of rubber to cellulosic fibrous material containing esterifiable OH groups is obtained if the latter is treated with an aliphatic $\alpha\beta$-unsaturated carboxylic acid or its anhydride or halide, e.g. crotonic acid or maleic anhydride, before applying the rubber and vulcanising.   C. O. C.

Acid Colloids of Resins. American Association of Textile Chemists and Colorists, Rhode Island Section. (III, p. 331.)

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Some Variables in the Colouring of Paper. F. North. *Proc. Tech. Sect. Paper Makers' Assocn.*, **29**, 127–157 (June 1948).

A review of the literature is followed by a description and discussion of experimental work on dyeing bleached sulphite pulp with three types of dyes. Variation in depth of shade of sized and unsized stock, the effect of varying pH with constant rosin and alum, with constant rosin and varying alum, with no rosin and varying alum, and with varying rosin and constant alum, as well as the influence of time of colouring and of varying furnish, were all investigated. It is concluded that the process of colouring paper consists essentially of two stages, the adsorption of dye from solution by the cellulose before the addition of sizing agents and, after their addition, the formation of a complex precipitate, the retention of which by the fibres completes the colouring process. The initial adsorption is negligible, small, and extensive with most acid, basic, and direct dyes respectively, and has been thoroughly investigated in the past. The effect of pH variations on retention can be explained to some extent by assuming the dye to be adsorbed by hydrous alumina, produced by hydrolysis of the aluminium sulphate on dilution. The theory is, however, practically contradicted by the effect of rosin on the retention of acid dyes. Data on the effect of pH, the most important single variable in paper colouring, are given in an appendix.   S. V. S.

Cellulose Ester Solutions. C. R. Fordyce and D. R. Simonsen. *Ind. Eng. Chem.*, **41**, 104–111 (Jan. 1949).

An understanding of the mechanism of evaporation of solvent mixtures containing cellulose derivatives has been sought with a view to controlling the properties of surface coatings. In the absence of cellulose derivatives, evaporation occurs primarily according to liquid–vapour equilibrium characteristics during exposure to atmospheric conditions. Evaporation deviates from this behaviour in presence of cellulose esters showing retention of certain types of solvents.   G. L.
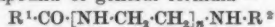
Preparations of Monocarboxycellulose and its Esters. M. Treyvas, N. Shorygina, and Z. Rogovin. *J. Appl. Chem. (U.S.S.R.)*, **22**, 1214–1224 (Nov. 1949).

Further experimental data are given regarding the formation and properties of monocarboxycellulose and its acetic and nitric esters, these substances being compared with the analogous pectic and alginic acids and their derivatives. The results support the general conclusions already published (cf. J.S.D.C., **66**, 91 (Jan.), 250 (April 1950)) and the proposed scheme of inter- and intra-molecular linkages is now given in greater detail. The rate of acetylation of monocarboxycellulose is very much less than that of the original cellulose, and this was at first attributed to the fact that, after a short initial period, the reaction with cellulose is a homogeneous one. However, when the reaction is carried out in a medium in which neither cellulose nor cellulose acetate is soluble, there is still a considerable difference in reaction rate. It is considered that during acetylation monocarboxycellulose forms a mixed polyuronic–acetic anhydride. Cross-links are then readily formed with neighbouring chains with the elimination of acetic acid, and these hinder the swelling, and hence the further progress of the reaction.   A. E. S.
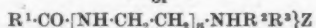
PATENTS

Wax Sizing of Paper. L. R. Sherman and Nopco Chemical Co.   *U.S.P.* 2,487,899.

Paper pulp is heated to above the m.p. of wax, wax is added, and after it has melted and been mixed with the fibres a compound of general formula—

$$R^1 \cdot CO \cdot [NH \cdot CH_2 \cdot CH_2]_n \cdot NH \cdot R^2$$

or

$$R^1 \cdot CO \cdot [NH \cdot CH_2 \cdot CH_2]_n \cdot NHR^2 R^3\}Z$$

(R^1 = a C_{7-23} aliphatic chain; R^2 = H or a C_{1-3} hydroxy-alkyl group; n = 2 or 3 when R^2 = H or 1–3 when R^3 = hydroxyalkyl; R^3 = H when R^3Z = a C_{1-3} aliphatic monocarboxylic acid or a C_{1-3} alkyl group when R^3Z = an ester of a mineral acid with a C_{1-3} aliphatic alcohol; Z = residue of an acid or ester), e.g. N-(hydroxyethylamino-ethyl)stearamide. All the wax is fixed on the fibre, so that the finished paper is smooth and free from wax spots.
    C. O. C.

Stabilised Dry Saponified Rosin Sizes. A. C. Dreshfield and Hercules Powder Co.   *U.S.P.* 2,488,385.

A non-dusting size which is readily dispersed in water consists of saponified rosin with 5–35% of a wax and enough of a compound of formula $R^1 \cdot NH \cdot R^2$ (R^1 = phenyl, naphthyl, lower alkylphenyl, lower alkoxyphenyl, lower alkylalkoxyphenyl, or lower alkylnaphthyl; R^2 = R^1 or tetrahydronaphthyl, *cyclo*hexyl, hydrocarbon-subst. *cyclo*hexyl, lower alkyl, lower hydroxyalkyl, or N-aryl-aminophenyl), e.g. N-methyl-β-naphthylamine, to prevent air oxidation.   C. O. C.

Water-borne Aluminium Coatings on Paper. S. J. Johnson and S. D. Warren Co.   *U.S.P.* 2,491,113.

A paper coating composition comprises aluminium flake casein, urea, sodium pyrophosphate, and as an insolu-bilising agent for the casein 5–20% (on the weight of casein) of dimethylolurea.   C. O. C.

XIII— RUBBER; RESINS; PLASTICS

The Superpolyurethanes. M. Souvé. *Chim. et Ind.*, **62**, 451–460 (Nov. 1949); **62**, 570–574 (Dec. 1949); **63**, 43–47 (Jan. 1950).

A review of the numerous industrial products based on the superpolyurethanes, and of the German firms which have manufactured them. A historical introduction is followed by a section on intermediate products, which are dealt with under poly*iso*cyanates (e.g. Desmodur T is a 60:40 mixture of toluene-2:4- and -2:6-di*iso*cyanate), and hydroxy polyesters. Then comes a comprehensive description of the preparation and synthesis of the principal types of polyurethanes, viz. polymers suitable for moulding, spinning, elastic purposes, lacquers and varnishes, adhesives, and plastic sponges. This is succeeded

by a detailed account of their properties, with illustrative curves and X-ray diagrams. Finally come the various industrial uses, with a short discussion of the patent literature, and with a bibliography of 18 references.

H. H. H.

PATENTS

Plasticisers for Polyvinyl Chloride. Compagnie Française de Raffinage.   *B.P.* 632,922.

Polyvinyl chloride resins of good mechanical properties are obtained by incorporating compounds of the type—
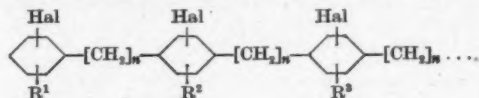
(R^1, R^2, R^3 = Alk or H; n = an integer), e.g. trichloro-p-phenylethyldiphenylethane.   W. G. C.

Stabilisation of Vinyl and Vinylidene Chloride Resin Compositions. British Resin Products Ltd., F. S. Deutsch, and L. H. P. Weldon.   *B.P.* 634,669.

A heat- and light-stable resinous composition comprises a synthetic resin including in its molecular structure a multiplicity of vinyl chloride and/or vinylidene chloride units and 0·5–10% by wt. of a bismuth salt of an organic acid containing not < 12 C atoms, e.g. bismuth stearate.

J. W. B.

Pigmented Polystyrene. E. D. Morris, S. S. Drake, and Dow Chemical Co.   *U.S.P.* 2,489,226.

Heat-plasticised polystyrene is milled with 10–25% of an insoluble pigment until a homogeneous dispersion is produced. This dispersion is then dissolved in liquid monomeric styrene together with enough polystyrene to yield a product of viscosity not < 35 centipoises at 25°c., and then the styrene is polymerised. The product is uniformly pigmented polystyrene.   C. O. C.

Production of Polyesters. J. G. N. Drewitt and J. Lincoln.   *B.P.* 634,609.

Polyesters are prepared by heating > 2 mol. of a halogenohydrin of a volatile glycol, e.g. ethylene chlorohydrin, with 1 mol. of a salt of a strong base and a dicarboxylic acid which is a pp'-dicarboxy derivative of a compound containing 1 benzene ring or 2 benzene rings linked directly or through C, O, or S atoms. Heating is continued till no unreacted carboxylic salt remains, halide by-product and halogenohydrin are separated, and finally glycol is evaporated until a polyester is obtained. The products are useful in coating compositions and when of sufficiently high mol. wt. can be spun into filaments.

J. W. B.

Rubber- or Leather-like Cured Polyester-Polyamides. D. W. Jayne, H. M. Day, E. L. Kropa, and American Cyanamid Co.   *U.S.P.* 2,490,001–5.

Plastic Fungicidal Composition. H. E. Smith and Insl-X Corpn.   *U.S.P.* 2,490,100.

Phenylmercury salicylate is an excellent fungicide for use with plastic compositions, as it is soluble in most plasticisers, non-ionising, chemically and thermally stable, insoluble in water, and relatively non-toxic.   C. O. C.

Fungicide for Plastics. H. E. Smith, W. Harden, and Insl-X Corpn.   *U.S.P.* 2,491,287.

A 25–50% solution of a phenylmercuric carboxylate in hydrogenated castor oil is useful as a fungicidal plasticiser for use with plastics.   C. O. C.

XIV— ANALYSIS; TESTING; APPARATUS

Dissociation Constants of very Weak Acids. N. Konopik and O. Leberl.   *Sitzungsber. Öster. Akad. Wiss.*, 158, (7–8), 655–669 (1949).

pH-Values of different concentrated solutions of mono- and di-sodium glucosate, di-sodium salicylate, Na_2HBO_3, Na_3BO_3, Na_3PO_4, and Na_3AsO_4, i.e. within the range 10–15, have been colorimetrically evaluated to $\Delta pH < 0·05$. The corresponding acid dissociation constants have been calculated from the pH values, and the method of calculation is discussed.   H. H. H.

Inorganic Chromatography on Cellulose. II— Separation and Detection of Metals and Acid Radicals on Strips of Absorbent Paper. F. H. Burstall, G. R. Davies, R. P. Linstead, and R. A. Wells.   *J.C.S.*, 485–490 (Feb. 1950).

Methods for the separation and detection of the metals constituting the ordinary qualitative analytical groups are described, and the isolation of the constituents of mixtures containing some of the less common metals (viz. U, V, Ti, Pt, Pd, Rh, Ir, Ru, Os, Au, Sc, Th) is also included. A few separations of anions ($SeO_3{}^{2-}$, $TeO_3{}^{2-}$, F^-, Cl^-, Br^-, I^-) have also been achieved. These methods are based on extraction with organic solvent mixtures on strips or sheets of absorbent paper; and detection is made by spraying the strip or sheet with a solution of suitable reagents, when the presence of individual metals or acid radicals is rendered visible by characteristic coloured bands. The ratio of the distances moved by ion and solvent (R_F value) has been determined in a number of cases, and its significance is discussed.   H. H. H.

Photometric Determination of Small Amounts of Fluorine with the Aluminium Lake of Eriochrome Cyanine. F. Richter.   *Chem. Tech.*, 1, 84–90 (1949): *Chem. Abs.*, 44, 971 (10th Feb. 1950).

Simple or complex F ions decolorise the aluminium lakes of Eriochrome Cyanine, and this reaction is utilised in a method for the accurate determination of very small amounts of F.   C. O. C.

Some Applications of a Modified Technique in Paper Chromatography. L. Rutter.   *Analyst*, 75, 37–42 (Jan. 1950).

A paper chromatographic method is described for the separation of the components of mixtures into circular zones, which has the advantage of speed, simplicity of apparatus, and reproducibility. Some new methods of detecting colourless adsorbates are outlined, and examples are given of the application of the technique to the analysis of dyes and inorganic substances. It would appear that solvents in which components show the greatest difference of solubility are desirable, and that, for adsorption of non-polar or only slightly polar compounds, a solvent in which they have a low solubility is desirable. H. H. H.

An Equation of the Comparison of Surface Tensions by Unstable Pendant Drops. K. G. Parvatikar.   *Current Sci.* (India), 18, 288 (1949): *Chem. Abs.*, 44, 889 (10th Feb. 1950).

The condition for similar shapes of two drops of any liquid from tips of different radii r_1, r_2 is that the quantity β for each radius be equal ($\beta = 2b^2/a^2$; $b =$ radius of curvature, $a =$ capillary constant). The proportionality of all corresponding linear dimensions is expressed by: $b_1/b_2 = a_1/a_2 = r_1/r_2$. Subscripts 1 and 2 refer to similar drops of two different liquids. If the contact angle between the liquid and the surface of a conical tip is the same, then the drops are similar in shape at the unstable stage—

$$\beta = \frac{g\sigma_1 b_1{}^2}{\gamma_1} = \frac{g\sigma_2 b_2{}^2}{\gamma_2}$$

The ratio of the surface tensions of two liquids can be calculated from the following equation—

$$\frac{\gamma_1}{\gamma_2} = \frac{\sigma_1 b_1{}^2}{\sigma_2 b_2{}^2} = \frac{\sigma_1 (de_1)^2}{\sigma_2 (de_2)^2}$$

($\sigma =$ effective density, $\gamma =$ surface tension, and $de =$ the equatorial diameter).   C. O. C.

Radioactive Method for Measuring the Adsorption of Dissolved Substances on Liquid Surfaces. G. Aniansson and O. Lamm.   *Nature*, 165, 357–358 (4th March 1950).

The method now described is based on the use of isotopes emitting non-penetrating radiations, like α-emitters and the soft β-emitters such as ^{14}C, ^{35}S, ^{45}Ca, and ^3H. A thin-window bell-type Geiger–Müller tube is placed immediately above a circular cup filled exactly to the brim with a solution of the surface-active compound tagged with the built-in radioactive isotope or with a solution of a radioactive ion. The Geiger–Müller tube counts the particles from the surface-adsorbed molecules or ions, and also those from the interior of the solution. However, the fraction of the particles from the interior decreases rapidly with depth, so that the count practically gives those from the adsorbed layer. The method applied to $C_{18}H_{37}SO_4Na$, labelled with ^{35}S, gave the quantity adsorbed on the

surface as $6\cdot05 \times 10^{-10}$ moles/sq. cm. in a $1\cdot6 \times 10^{-5}$ N. solution at 18°c.   H. H. H.

Evaluation of Wetting Agents. L. Shapiro. *Amer. Dyestuff Rep.,* 39, P 38–P 45, P 62 (23rd Jan. 1950).

A modified "Draves test" is described and discussed. A standard tape is used to replace the skein and the weight is altered suitably for the experimental conditions. Experimental comparisons were made with the Draves test and extensive experiments were carried out to determine the effect of altering the weight. Among the advantages over the former which this method gives are reproducibility, greater ease of handling tape, and the use of the same test solution for a greater number of experiments. All of these tend to increase the speed of the test. There appear to be no disadvantages.   W. J. M.

Separation and Purification of Organic Substances by Sublimation over Adsorption Reagents. W. Kofler. *Sitzungsber. Öster. Akad. Wiss.,* 158, (7–8), 694–701 (1949).

The method described in a combination of adsorption methods of gas analysis with the Tswett process of chromatographic analysis, the substances being sublimed under reduced pressure and usually at a temperature below the m.p., with a carrier gas, and adsorbed in a heated column, for which silica gel, Floridin XS, or active charcoal may be used. The column is then treated with a regulated current of air or indifferent gas during a slow temperature increase, whereby the substances are separated during a period of 2–3 hr. Examples cited are the purification of *o-, m-,* and *p*-nitroaniline, *m*-aminophenol, *p*-nitrophenol, 1:2-benzanthracene, and α-naphthylamine; and the separation of mixtures of benzoic and cinnamic acids, azobenzene and salicylic acid, *o-* and *p*-nitroaniline, *m-* and *p*-nitroaniline, and 2:4:6-trichloro- and -tribromo-phenol.   H. H. H.

Hydrogen Bonding and Chromatographic Separability of Isomeric Compounds. H. Hoyer. *Kolloid-Z.,* 116, 121 (Feb. 1950).

Molecules with internal hydrogen bonding will be more soluble in non-polar substances than those in which such bonding is absent. This viewpoint has been verified in the hydroxyanthraquinone series, in which those members with hydroxyl groups in the 1-, 4-, 5-, and 8-positions, and thus capable of hydrogen bonding, can flow easily through silica gel when dissolved in benzene, chlorobenzene, and methylene chloride, whereas their isomers with hydroxyl groups in other positions are adsorbed. The Winterstein rules (*Hoppe-Seyler's Z. physiol. Chem.,* 220, 247 (1933)) on the degree of adsorption as a function of the hydroxyl group number and on depth of colour are found to be invalid. Thus solutions of 1:4:5-tri- and 1:4:5:8-tetra-hydroxyanthraquinone pass through the silica gel column with ease; whereas 2-hydroxyanthraquinone is adsorbed. Moreover, 1:4:5:trihydroxyanthraquinone has a deeper colour than the adsorbable 1:3:5-isomeride. The same properties occur in the nitrohydroxy and hydroxyazo compounds.   H. H. H.

Studies on Coaltar Colours. VI— D&C Red No. 14, 15, 16, and 31. VII— D&C Red No. 34. K. A. Freeman and C. Stein. *J. Assocn. Offic. Agr. Chemists,* 32, 718–726 and 726–731 (1949): *Chem. Abs.,* 44, 841 (25th Jan. 1950).

VI— Purified samples of D&C Red No. 14 and 15 and their colour acid, 1-(2′-carboxyphenylazo)-2-naphthol, and of D&C Red No. 31 and its colour acid, 1-phenylazo-3-carboxy-2-naphthol, were prepared and studied spectrophotometrically. The data obtained have been applied to the determination of "pure colour" in commercial samples of D&C Red No. 16, Barium Lake, and to D&C Red No. 31, Calcium Lake.

VII— Spectrophotometric data suitable for application to the determination of the "pure colour" in commercial samples of D&C Red No. 34, Calcium Lake, are given as obtained from purified samples of D&C Red No. 34.   C. O. C.

Reaction for Amino and Imino Groups in Textile Materials. G. R. Wellin. *Amer. Dyestuff Rep.,* 38, 746 (17th Oct. 1949).

Attention is directed to the method of Tarugi and Lenci for the determination of $-NH_2$ and $=NH$ groups, which although developed in 1912 has not received wide usage. As a very sensitive qualitative test a few crystals of phenol

are placed on the material, and a few drops of alkaline sodium hypochlorite (>3% available chlorine) added. An intense blue colour is formed in the presence of substances containing the above groupings.   W. K. R.

Practical Tests for Quantitatively Evaluating Dye Characteristics and Dyeing Methods. American Assocn. of Textile Chemists and Colorists, Northern New England Section. *Amer. Dyestuff Rep.,* 38, P 812–P 815, P 827 (14th Nov. 1949).

By means of tests which measure exhaustion, strike, penetration, and levelling, it is possible to predict the relative performances of dyes, dyeing methods, dyeing assistants, and textile materials. Details are given for measuring quantitatively these four characteristics.

      A. S. F.

Measurement of Colour. G. G. Taylor. *Proc. Tech. Sect. Paper Makers' Assocn.,* 29, 409–430 (Dec. 1948).

The theory of colour and its measurement is briefly discussed, and this is followed by descriptions of the Ogal (Duboscq-type) colorimeter, the Spekker photoelectric absorptiometer, the Hardy spectrophotometer, and the Lovibond Tintometer and their applications.   S. V. S.

Standard Solutions for Humidity Control at 25°C. R. H. Stokes and R. A. Robinson. *Ind. Eng. Chem.,* 41, 2013 (Sept. 1949).

The concentrations of solutions of sulphuric acid, sodium hydroxide, and calcium chloride required to produce relative humidities within the range 5–95% at 25°c. are given, and also data for the relative humidities above sixteen saturated salt solutions at 25°c. The figures are based on careful recent determinations.   W. K. R.

Solutions for Maintaining Constant Relative Humidity. D. S. Carr and B. L. Harris. *Ind. Eng. Chem.,* 41, 2014–2015 (Sept. 1949).

The aqueous tensions maintained by twelve saturated aqueous salt solutions (the halides of sodium and potassium., sodium nitrate, nitrite, chromate, and dichromate, and chromic oxide CrO_3) in an enclosed space from room temp. to 90°c. are given, along with the relative humidities ca.ulated therefrom.   W. K. R.

Note on the Theory of the Lepidometer. K. R. Makinson. *J. Textile Inst.,* 40, T 809–T 812 (Dec. 1949).

From a theoretical analysis of the action of the lepidometer it is shown that the quantity measured lies between the difference σ_{ss} between the coefficients of static friction with and against the scales and the difference σ_{sk} between the against-scale coefficient of static friction and the with-scale coefficient of kinetic friction. Since, except in the case of heavy lubrication, $\sigma_{sk} > \sigma_{ss}$, the quantity measured is greater than σ_{ss}, so that the instrument exaggerates small frictional differences. It is considered that the quantity measured, however, is probably related to the tendency of the mass of fibres to felt, the closeness of this relation depending on the mechanical constants of the lepidometer.   W. K. R.

Relationship between Results of Dynamic Absorption Tests using Hexagonal and Cylindrical Jars. M. I. Landsberg, C. Sembach, and R. Blum. *Amer. Dyestuff Rep.,* 38, 744–746 (17th Oct. 1949).

The standard hexagonal jar in which patterns are shaken in the dynamic absorption test for water-repellency has been replaced by a more convenient cylindrical jar $6\frac{1}{4}$ in. in diameter and $11\frac{3}{4}$ in. long. Test results are unaffected by the change.   W. K. R.

Determination of Chlorine Pick-up. E. R. Atkinson and N. A. Sargent. *Amer. Dyestuff Rep.,* 38, 743 (17th Oct. 1949).

Fabrics treated with certain resins retain chlorine in the form of N-chloroamines on bleaching with sodium hypochlorite. The amount of chlorine so retained is determined by stirring a 10-g. fabric sample in 500 ml. of a 1% solution of potassium iodide and titrating the liberated iodine, as formed, with $0\cdot01$ N. sodium thiosulphate. Practically all the retained chlorine reacts within 8 min.   W. K. R.

Chromatography of Soluble Starches. M. Ulmann. (III, p. 331.)

Note on the Disintegration of Wool in Abrasion Tests. H. F. Schiefer and J. F. Krasny. (VI, p. 338.)

Effect of Copper Salts on the Fastness of Vat Dyeings. J. P. Niederhauser. (X, p. 341.)

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